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# Sources and Transport of Trace Metals in Urban Aerosols

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Aerosol characterization studies were focussed on St. Louis, Missouri, during the Regional Air Pollution Study. Trace element pollutants were distinguished from their natural components on the basis of particle size distributions. Statistical analysis of time-sequenced concentration measurements revealed four distinct pollution sources for lead. A related analysis demonstrated that meteorological factors controlling the transport of titanium aerosol across the city could be identified. Extensions of the meteorology were applied to (1) the determination of trace element pollution deposition in the human respiratory tract through direct sampling of exhaled breath, (2) indoor environments, and (3) nonurban continental and marine atmospheres.

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# SOURCES AND TRANSPORT OF TRACE METALS IN URBAN AEROSOLS

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A methodology was developed, tested, and applied to the identification of trace element aerosol sources and trace element aerosol transport phenomena. The method uses lightweight and portable field sampling equipment and results in the acquisition of large data sets suitable for statistical analysis and the testing of aerosol transport models. Aerosol sampling in the ambient atmosphere was accomplished through a combination of time-sequenced filter collections with hourly resolution, and fractionated aerosol collections with 0.25 μm resolution. Elemental analysis was performed with particle induced X-ray emission, a sensitive and rapid method.

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Extensions of the methodology were applied to (1) determination of trace element pollutant deposition in the human respiratory tract through direct sampling of exhaled breath, (2) the indoor environment by comparison of time variability in elemental concentrations with those measured outdoors, and (3) nonurban continental and marine atmospheres.

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CONTENTS


Abstract . . . . . iii
Acknowledgment . . . . . vi

1. Introduction . . . . . 1
2. Conclusions . . . . . 3
3. Trace Metal Identification Techniques . . . . . 6
   PIXE principles . . . . . 6
   PIXE spectrum resolution . . . . . 10
4. Sampling the Urban Aerosol . . . . . 15
5. Clues to the Sources of Trace Metals in Urban Aerosols . . . . . 22
   Evidence from particle size distribution . . . 22
   Meteorological analysis of the titanium pollution plume . . . . . 30
   Lead, a multiple source pollutant in St. Louis . . . . . 34
6. Aerosol Properties and Human Respiratory Exposure . 40
   Respiratory response in aerosol inhalation . . 40
   The fate of lead aerosol along a roadway . . . 44
   Lead aerosol in the indoor residential atmosphere . . . . . 48
7. Aerosol Transport out of the Urban Source Region . 51
   The north Florida coastal zone . . . . . 51
   Air pollution present in the North Atlantic marine atmosphere at Bermuda . . . . . 54

References . . . . . 58
List of Publications and Reports . . . . . 59

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# SECTION 1

# INTRODUCTION

The suspended particulate matter of urban atmospheres contains substantial quantities of trace metals together with sulfates, organic matter, and other non-metallic constituents. Trace metals, of course, occur naturally since all of them are constituents of naturally occurring dust which originates from materials at the earth's surface. However, urban activities, including the combustion of fuels, industrial processes, and the motions of vehicular traffic which tend to raise surface dust, are activities which tend to increase the concentrations of certain trace metals in the atmosphere above their natural levels.

Some trace metals play an active role in the metabolism of man and other living things, and some metals, when present to excess, may be toxic to man. Trace metals may also play an active role in the chemistry of the atmosphere, for example by acting as catalytic substrates for chemical reactions that convert gaseous into particulate material. Such may be the case for some metal oxides which may accelerate the conversion of sulfur dioxide to sulfates or may facilitate the condensation of organic vapors into small liquid droplets.

For these reasons a thorough investigation of the contents of trace metals in urban atmospheres is needed for setting optimum air pollution control strategies. Such an investigation should seek to find ways to identify the sources of individual trace metal constituents of the particulate matter and the factors which determine the extent of transport of these metals from their sources to other atmospheric locations and eventual removal from the atmosphere.

The atmosphere in most cities contains particulate matter derived from a multiplicity of sources. Seldom does one find an element which is derived predominantly from one source type, but rather any trace metal may enter the atmosphere from a number of different processes and types of human activity. Therefore it is not a straightforward task to identify the sources of trace metals by measuring their concentrations in the atmosphere. Indeed, it is also not straightforward to determine unambiguously whether the measured trace metal concentrations in the urban atmosphere are higher than their natural levels.

## SECTION 2

## CONCLUSIONS

1. The method of proton induced X-ray emission analysis, PIXE, is extremely precise and sensitive for the measurements of trace metal concentrations in atmospheric aerosol samples. It has been successfully calibrated and intercompared with other analytical methods for absolute accuracy of the order of 10%.

2. The PIXE method permits the use of small portable aerosol sampling equipment which can be economically deployed over networks on the urban scale. The small area of the analyzed portion of a sample permits use of miniature vacuum pumps with modest electrical power requirements. Thus, large scale aerosol sampling programs may be carried out with greater versatility and lower costs than if larger field sampling equipment were required.

3. Particle size distribution measurements can be made by sampling particle size fractions with cascade impactors. Impactors compatible with the PIXE method provide 6 particle size fractions, <0.25 μm, 0.25-0.5 μm, 0.5-1 μm, 1-2 μm, 2-4 μm and >4 μm aerodynamic diameter. The size range below about 4 μm, which comprises most of the particle mass for several trace metals of pollution importance, includes the respirable size range over which it is important to determine the distribution of elemental composition. Not only is this information desirable from a health effects standpoint, but it also assists in the identification of different pollution source processes for atmospheric trace metals.

4. Measurements of the time variability of aerosol trace metal concentrations with hourly time resolution can be made conveniently with the continuous time sequence "streaker" filter sampler. This time resolution is matched to the scale of important variability in the atmospheric motions that control the transport of aerosols over the urban dimensions. With time variability information transport models may be tested, and specific pollutants may be identified as useful transport tracers.

5. In St. Louis, trace metals from low temperature pollution sources may occur primarily in particles larger than 1 μm aerodynamic diameter; whereas high temperature sources

preferentially emit submicrometer particles to the atmosphere. For example, automotive lead aerosol particles are significantly smaller than those of smelter lead aerosol. Industrial iron aerosol appears to have a larger component of submicrometer particles than iron derived from soil or other dust.

6. A local titanium pollution source in St. Louis causes elevated titanium concentrations throughout the St. Louis urban area. The concentrations show variations which are strongly dependent on wind direction, variability in mean wind direction, wind speed, atmospheric temperature gradient, land and water differences, and the occurrence of precipitation. The time variability pattern of titanium observed at different measurement stations has been used to evaluate quantitatively the importance of these factors in governing the titanium transport. In principle other trace elements and their associations may also be used as tracers to test transport mechanisms from stack emissions in the urban area in a manner similar to that demonstrated for titanium.

7. The association of lead with other trace metals in the St. Louis atmosphere has been analyzed statistically to demonstrate the existence of four different pollution components of atmospheric lead. These are the automotive component with a strong bromine correlation, a zinc related component possiby from smelter emissions, a crustal element related component possibly from fly ash, and an independent component possibly from secondary lead smelting, showing no other elemental association.

8. The high sensitivity of the PIXE method permits the sampling of exhaled human breath aerosol in normally polluted atmospheres by means of cascade impactors. Comparison of breath with ambient aerosol particle size fractions has enabled us to estimate the efficiency of particle deposition in the human respiratory tract as well as a humidification response on inhalation. The fact that a minimum deposition efficiency is observed for particles in the range 0.25-0.5 μm or possibly smaller points to the importance of particle size resolution in this range when evaluating potential health effects of pollution aerosols.

9. Streakers and cascade impactors have been used for monitoring lead, sulfur, and other elements along a heavily travelled roadway. Particle size of lead aerosol is found to be significantly greater for aged air parcels compared to air from the traffic lanes, an observation of importance to estimating human respiratory deposition of lead. Aged air is also characterized by a lower Br/Pb ratio than that of fresh automotive aerosol, suggesting bromine loss from the particles during atmospheric transport.

10. Indoor air pollution has been monitored directly with the streaker sampler and compared with outdoor concentrations. A detailed study of the correspondence in time variability patterns for certain residential atmospheres has established that lead and sulfur generally penetrate indoors from the outdoor urban atmosphere but that potassium has significant indoor sources. Some evidence has also been obtained indicating that a portion of the lead observed indoors may be due to recirculated contaminated household dust.

11. Measurements in nonurban continental and marine atmospheres have been made to evaluate the natural atmospheric concentrations with which the urban atmosphere may be compared. It is noteworthy that at Bermuda, more than 1000 kilometers from the eastern U.S. seaboard, fine particle sulfur aerosol was found to be many times above its level at highly remote sites in the Southern Hemisphere and indicates substantial long-range transport of pollution out over the Atlantic from the North American continent.

## SECTION 3

## TRACE METAL IDENTIFICATION TECHNIQUES

The measurement of trace metals in urban air particulate matter requires highly sensitive detection methods in order to measure the small quantities of each metal that may occur in samples collected over short periods of times. Furthermore, valuable clues concerning the sources of trace metals may be obtained by examining the distribution of concentration over different particle size ranges. Since sampling devices for short sampling intervals and for particle size selection gather only small amounts of suspended particulate matter, a high degree of sensitivity is required for a suitable elemental analysis technique.

The method of particle induced X-ray emission, using protons accelerated by a Van de Graaff accelerator up to 5 MeV, provides sensitivity for accurate measurements of many of the important trace metals in urban atmospheres down to a nanogram or less of each metal. Furthermore, this method is best used to analyze samples of very small dimensions, a few $mm^2$ or less, and those samples which are collected conveniently by time sequence and particle size fractionating devices. This method, known as PIXE, is the method of choice for obtaining the atmospheric chemical information described here.

### PIXE PRINCIPLES

In principle, PIXE involves the bombardment of a sample for a minute or so in the vacuum chamber of a particle accelerator so as to generate X-rays characteristic of each element in the sample. These X-rays are detected by a solid state lithium drifted silicon detector, Si(Li). Electrical pulses from the detector are transformed electronically into signals recorded on a magnetic tape. After a few hundred analyses have been performed and recorded on the magnetic tape, the tape records of X-ray spectra of the individual samples are resolved into the concentrations of the individual elements by a digital computer. Most of the techniques for aerosol sampling, PIXE analysis and computer X-ray spectrum resolution which have been used in the work reported here have been developed especially for the purposes of this study of trace metals in urban aerosol particulate matter.

**Table I. Results of Analysis of Thin Homogeneous Standard Samples**

| Element (compound) | Amount given, μg | PIXE results: Found, μg | Number of determinations | % Std dev per determination |
|---|---|---|---|---|
| Cl (NaCl) | 6.8 | 5.6 | 3 | 5.2 |
| Cl (KCl) | 6.3 | 6.6 | 7 | 6.7 |
| K (KCl) | 7.0 | 7.1 | 7 | 6.5 |
| Ca (CaF) | 3.7 | 3.6 | 5 | 9.8 |
| Ti metal | 10.2 | 8.9 | 3 | 9.0 |
| Cr metal | 7.2 | 7.1 | 5 | 1.0 |
| Fe metal | 11.5 | 13.7 | 5 | 3.1 |
| Cu (CuS) | 7.9 | 8.1 | 14 | 7.1 |
| Ga (GaP) | 4.6 | 4.6 | 2 | 7.8 |
| Br (CsBr) | 3.1 | 3.0 | 3 | 3.0 |
| Cs (CsBr) | 5.2 | 5.5 | 3 | 6.0 |

**Table II. Results from an Interlaboratory Comparison Study**

| | Sample on Millipore filter: Amount given, ng[a] | Sample on Millipore filter: Amount found[b] / Amount given | Sample on Whatman 41 filter: Amount given, ng[a] | Sample on Whatman 41 filter: Amount found[b] / Amount given |
|---|---|---|---|---|
| K | 2040 | 1.032 | 943 | 0.981 |
| V | 374 | 1.071 | 233 | 1.069 |
| Mn | 1649 | 1.022 | 693 | 0.915 |
| Fe | 1916 | 1.093 | 1269 | 0.988 |
| Cu | 300 | 1.110 | 202 | 1.151 |
| As | 356 | 1.154 | 244 | 1.120 |
| Pb | 813 | 1.064 | 558 | 1.083 |
| Mean | | 1.078 | | 1.044 |

[a] Given amount of each element within area of proton beam striking sample. [b] Ratio of PIXE result to given amount for 2 to 4 replicate determinations. The standard deviation for a single determination by PIXE is approximately 15%.

**Table III. Comparison between Heterogeneous and Homogeneous Samples**

| | Heterogeneous foil (~1 mm² piece) | Homogeneous foil |
|---|---|---|
| Zr-foil | 5.66 ± 0.53 mg/cm² | 5.01 ± 0.35 mg/cm² |
| Fe in Al-foil | 21.3 ± 2.0 μg/cm² | 23.3 ± 1.7 μg/cm² |
| Zn in Al-foil | 1.02 ± 0.15 μg/cm² | 0.80 ± 0.10 μg/cm² |

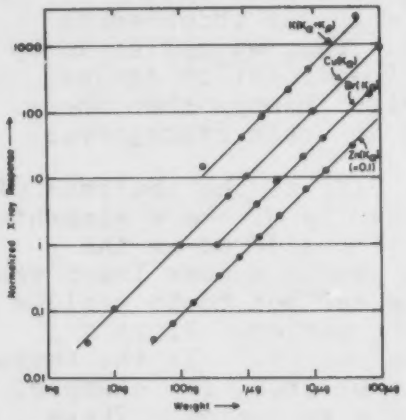



**Figure 5. Results from linearity tests**

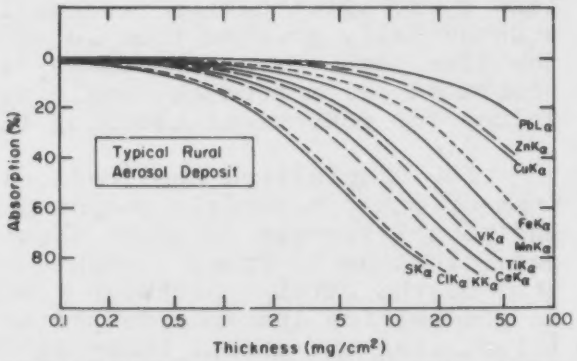



**Figure 6. X-Ray attenuation in a homogeneous sample as a function of sample thickness**

Source: A-2
Thomas B. Johansson, Rene E. Van Grieken, J. William Nelson, and John W. Winchester, Elemental trace analysis of small samples by proton induced X-ray emission, Anal. Chem., 47, 855-860, 1975.

In the development of the PIXE method a considerable amount of testing has been carried out to assure accuracy and reliability of the method. For example, Plate 1 shows in three tables that standard samples can be analyzed to an accuracy of 1 - 10% on an absolute basis. An interlaboratory comparison of PIXE method with the results obtained using other analytical methods at other institutions (Camp et al., 1974, 1975) shows an overall agreement for several trace metals of better than 10% on the average. We likewise have verified that the PIXE method is capable of analysis of a very small spot of sample as well as an evenly distributed wide area sample. This advantage is of special significance because it permits the analysis of individual particle size fractions collected by cascade impactors of the single orifice type which are described further below. This impactor collects samples as circular deposits of approximately 1 $mm^2$ diameter and requires the analysis of the entire sample spot. In the PIXE method the proton beam strikes a larger area which completely contains the spot and measures each trace metal contained within it.

Also shown in Plate 1, Figure 5, is a demonstration that the PIXE method permits a linear response of X-ray signal over at least a factor of 10,000 in amount of sample irradiated by the proton beam. A potential limitation to linearity is samples which are very thick and attentuate X-rays as they leave the sample after their proton induction. In Plate 1, Figure 6, a calculated absorption of X-rays in the sample shows that samples thinner than about 1 $mg/cm^2$ should give less than about 10% absorption for X-rays as soft as those for sulfur. More energetic X-rays are absorbed to a lesser extent so that lead X-ray attentuation reaches 10% only for thicknesses substantially greater than 10 $mg/cm^2$. Samples collected by the time sequence and particle size fractionation devices described below produce sample deposits thinner than these values for convenient sampling times in urban atmospheres.

For specialized applications of PIXE to the analysis of iron or other materials composed primarily of heavy elements, additional sources of error should be considered in the determination of trace elements with atomic number lower than that of the matrix, although these appear not to be serious in general for atmospheric particulate matter. Plate 2 illustrates the effect known as "enhancement," In the bombardment of a sample composed principally of iron, for example, considerable amounts of iron X-rays are generated. These X-rays may be critically absorbed by the trace metals also present in the sample and cause a secondary generation of their characteristic X-rays. Therefore the trace metal X-rays detected will be those not only due to the proton induction but also the secondary X-ray induction. As a result, a signal enhancement occurs which will cause an erroneously high analysis unless enhancement is corrected for. As indicated in

Plate 2

TABLE 1

Enhancement in % from the Fe $K_\alpha$ and Fe $K_\beta$ X-rays on $K_\alpha$ X-rays from different elements. Calculated for 2.5 MeV protons in a 100% iron sample.

| Z | Element | Exciting X-ray | |
|---|---|---|---|
| | | Fe $K_\alpha$ | Fe $K_\beta$ |
| 25 | Mn | 0 | 7.8 |
| 24 | Cr | 41 | 4.7 |
| 23 | V | 24 | 2.8 |
| 22 | Ti | 14 | 1.6 |
| 21 | Sc | 8.6 | 0.95 |
| 20 | Ca | 4.9 | 0.54 |
| 19 | K | 2.7 | 0.30 |
| 17 | Cl | 0.83 | 0.09 |

TABLE 2

Analysis of NBS low alloy steel SRM 1261 (95.6% Fe), with 5 MeV protons.

| Element | Concentration (%) | | |
|---|---|---|---|
| | No enhancement correction | With enhancement correction | N3S value |
| Mn | 0.80 | 0.71 | 0.66 |
| Cr | 1.24 | 0.71 | 0.69 |

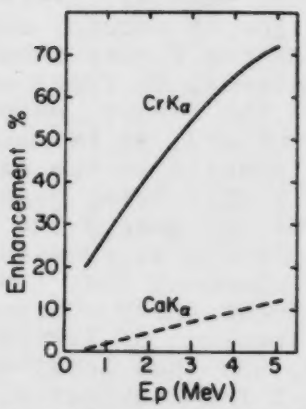



Fig. 2. Enhancement from Fe $K_\alpha$ X-rays on Cr $K_\alpha$ and Ca $K_\alpha$ X-rays as a function of proton energy in a 100% iron sample.

Source: A-4
Mats. S. Ahlberg, Enhancement in PIXE analysis, Nuclear Instruments and Methods, 142, 61-65, 1977.

Table 1 of Plate 2 the enhancement of chromium X-rays in an iron sample may be more than 40%. In a typical steel sample analyzed without enhancement correction the chromium analysis was found to be high, but if the enhancement correction is made, the analysis is in good agreement with the standard value. As seen in Figure 2, Plate 2, the enhancement problem becomes more severe at higher proton energies but is less severe for elements of considerably lower atomic number than the matrix, such as calcium in comparison with the matrix element, iron.

In aerosol analysis most major elements are of lower atomic number than the trace elements measured by PIXE. For example, more than half of the total particulate mass typically found in urban atmospheres is composed of the elements C, H, O, N, S, with additional Na, Mg, Al and Si, all of these being elements of atomic number lower than the trace metals whose concentrations are discussed further in this report. Even for the extreme case of measuring trace amounts of sulfur in pure rock salt, NaCl, calculations show that enhancement of sulfur X-rays is not a source of significant analytical error.

## PIXE SPECTRUM RESOLUTION

A crucial part of the PIXE analytical procedure, and one without which the method would not succeed, is the translation of the accumulated electronic signals from the Si(Li) X-ray detector into a list of elemental concentrations in the sample. This feat is accomplished by the unraveling of the X-ray spectrum, consisting of a number of X-ray counts recorded in each of 600 or more individual energy channels, into the contribution from each elemental constituent of the sample. Plate 3, Figure 2 shows a typical X-ray spectrum for an aerosol sample collected on a filter. The three parts of the figure show the effect of interposing a thin absorbing material in front of the Si(Li) detector window causing some of the X-rays, especially those of lowest energy (lowest channel number), to be absorbed. In both cases individual elements present in the sample account for peaks in the spectrum, but a thin Mylar plastic absorber skews the entire spectrum in the low energy end so that the elements Al, Si, and S are completely suppressed. In samples where these elements may be so abundant that their X-rays are intense enough to limit the permissible bombardment intensity of the sample by the proton beam (because of limitations on the speed of electronic circuitry), and thus lengthen the total analysis time required to detect the heaviest elements in the sample, this technique of using an X-ray absorber is useful. By suppressing these troublesome light elements, a more intensive proton bombardment is permitted, and shorter analysis time is required for accurate measurement of heavier metals, for example lead.

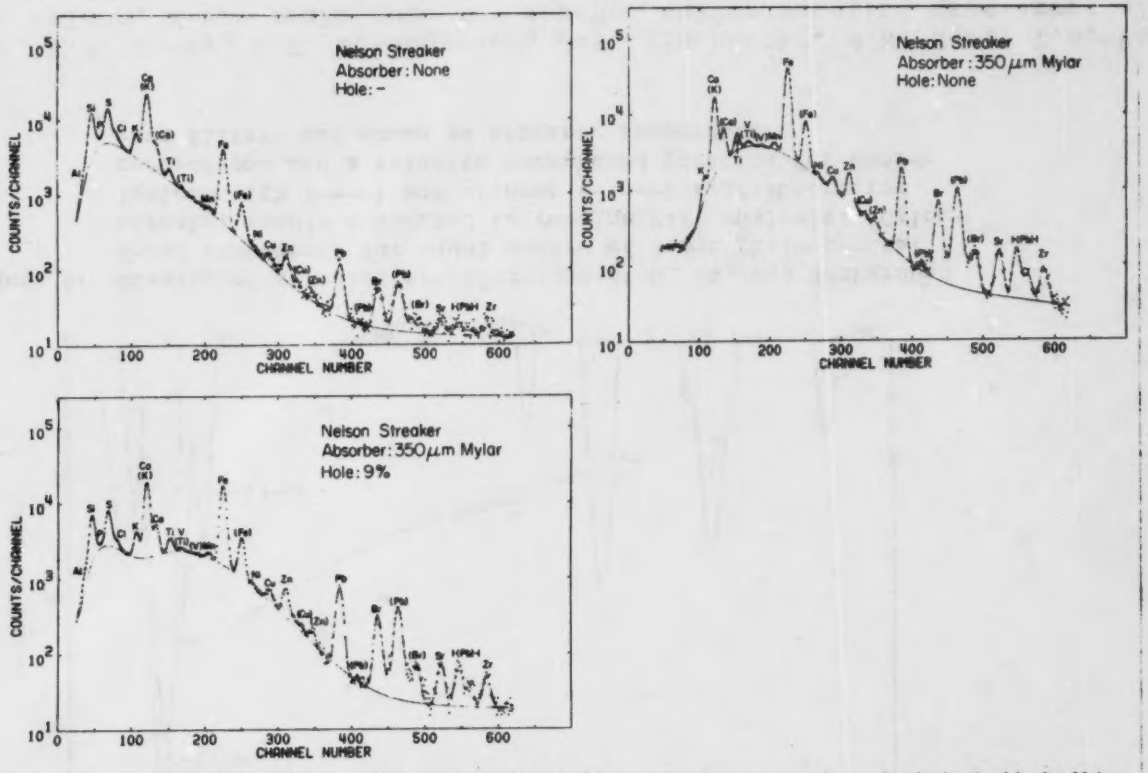



Fig. 2. Fits to proton induced X-ray emission spectra obtained from bombarding an aerosol sample obtained with the Nelson Streaker. For quantitative comparison see table 1.

Plate 3a

Source: B-8.
Henry C. Kaufmann, K. Roland Akselsson, and William J. Courtney, REX-a computer programme for PIXE analysis, Nuclear Instruments and Methods, 142, 251-257, 1977.

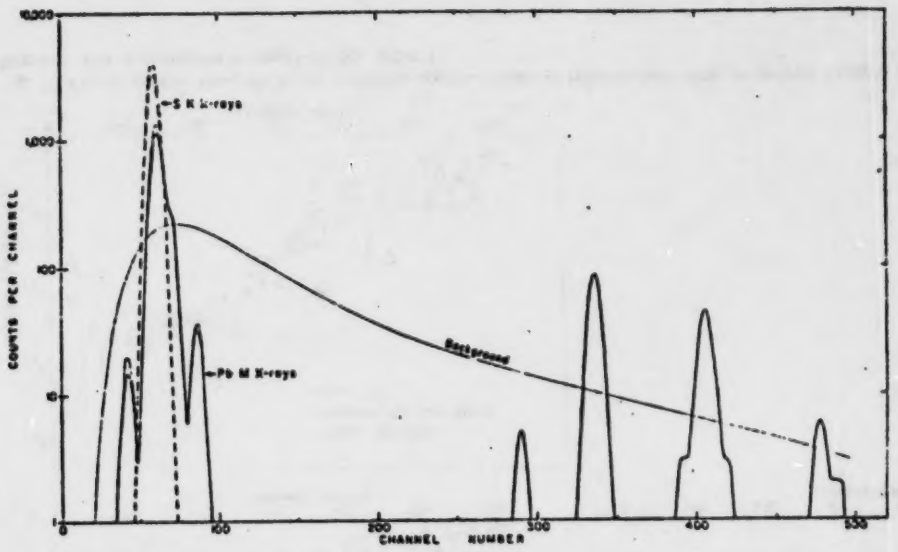



**Figure 4. Display of relative contributions of S, Pb, and background X-ray components for equal masses of S and Pb in typical streaker sample subjected to routine PIXE analysis. Calculations with (——) and without (-----) self-absorption corrections and a relative background position for Nuclepore filters are shown as separate components.**

Source: A-18.
K.R. Akselsson, K.A. Hardy, G.G. Desaedeleer, J.W. Winchester, W.W. Berg, T.B. Vander Wood, and J.W. Nelson, X-ray techniques for aerosol sulfur baseline assessment along an urban freeway, Advances in X-Ray Analysis, vol. 19, R.W. Gould, C.S. Barrett, J.B. Newkirk, and C.O. Ruud, eds., pp. 415-425, Kendall Hunt, Dubuque, Iowa, 1976.

A more usual case in aerosol analysis is where both the light and heavy elements must be determined, and therefore a complete suppression of the light elements is not desired. In that case the absorber is used as before but in a modified form, such that a small hole is cut in the center of the absorber in order to transmit without absorption a small fraction of the unattenuated X-rays; for example the spectrum using a 9% hole absorber is shown in Figure 2 of Plate 3. The light elements, which are completely suppressed by the remaining 91% of the absorber area, are seen as unattenuated X-ray peaks at 9% of the original intensity. The heaviest elements are effectively unattenuated by the thin absorber, as before. A few elements of intermediate character, in this case K and Ca, are partially attentuated by the absorber, but from calibration measurements their overall transmissions may be calculated. With this X-ray absorber the entire spectrum of elements from Al to Pb and beyond may be measured in a single bombardment lasting only a minute or so depending on sample size.

A practical case of potential X-ray interference between elements is illustrated for the case of measuring sulfur in the presence of lead. Along roadways where leaded gasoline is burned the concentration of atmospheric lead may be highest relative to sulfur in comparison with air anywhere in the urban environment. The lead X-ray spectrum contains many peaks, both in the higher energy region where the peaks are used for element identification and in the low energy region of the most important sulfur peaks. These low energy M X-rays of lead pose a potential interference in the accurate resolution of sulfur from the spectrum. The computer X-ray resolution procedure developed for this research removes the interference by accurately calculating the amount of lead present, estimating the low energy lead X-ray component, and determining the net sulfur X-ray present. Under normal circumstances the extent of lead X-ray interference in sulfur determination does not exceed a few percent, and even in a roadway situation the interference, whereas perhaps ten times greater, is still accurately measurable.

This example illustrates that the PIXE X-ray spectrum resolution problem requires a detailed evaluation of all physical relationships among the constituent elements in the sample. An especially important part of the problem is the accurate determination of the X-ray background contributed by the sample mass and the sample substrate, for example filter paper or particle impaction surface. This background is produced by atomic interactions during proton bombardment distinct from those which produce the characteristic X-rays of the elements. In the light element region of sulfur and neighboring elements the background X-ray spectrum exhibits considerable curvature, and in the case of the absorber with hole the curvature is of complex shape. If the concentrations of light elements are relatively

low, the estimation of their amounts above background requires an accurate measurement of the background. In the computer procedure we do not use separate measurements of substrate materials without sample, e.g. blank filters, nor direct measurement of the background since this would not include the mass effect of the sample itself in causing the background X-radiation. Instead, in our procedure the principal physical processes causing the background have been identified, and the background shape has been successfully modeled. Comparison with standard samples indicates that this modeling of the background permits accurate measurements of the important light elements. Thus the computer procedure for spectrum resolution requires only the data contained in the sample spectrum alone, and offers a great advantage in simplicity and speed of the computer data processing (normally about one minute per spectrum) and in overall accuracy.

## SECTION 4

## SAMPLING THE URBAN AEROSOL

A comprehensive investigation of trace metals in urban aerosols requires techniques for measuring their concentrations in air which will:

1. Provide a determination of trace metal distributions among particles of different size over the stable aerosol size range <0.25 μm to >4 μm aerodynamic diameter.

2. Provide an indication of the time variability of trace metal concentration on a time scale comparable to the 3-hour meteorological data provided by the National Weather Service.

3. Provide for the simultaneous measurement in each sample of several trace metals of air pollution interest so that inter-element correlations may be studied as indicators of sources and transport pathways.

4. Provide data sets of sufficient size for statistical methods of interpretation to be employed.

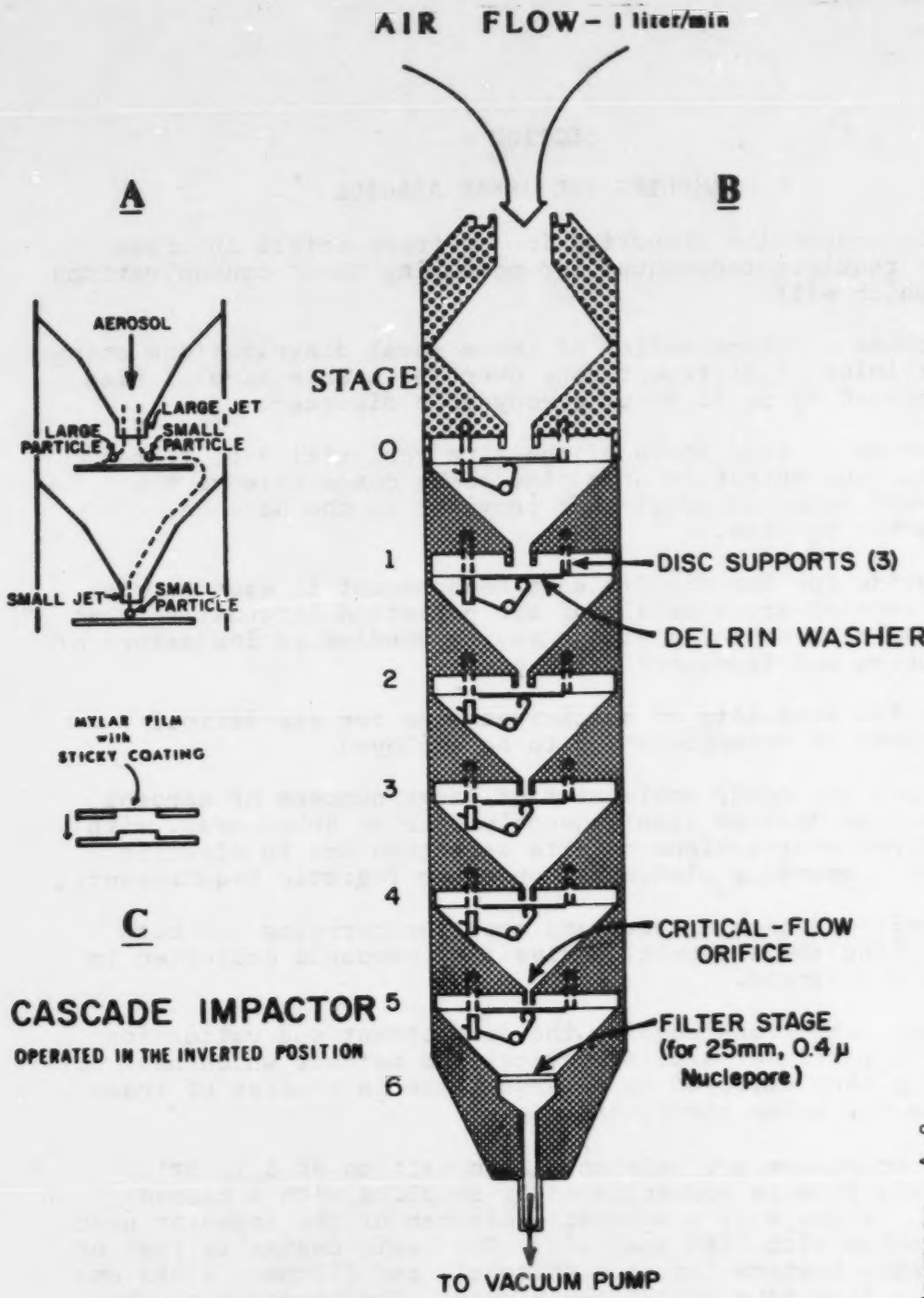
5. Permit the ready deployment of large numbers of aerosol sampling devices simultaneously over an urban area, with minimum restrictions on site selection due to electric power, mounting platforms, or other logistic requirements.

6. Permit reasonable speed and cost for carrying out both sampling and elemental analysis of aerosols collected in field programs.

These conditions require the development and validation of aerosol particle sampling devices and methods which have not previously been employed on a large scale in studies of trace metals in the urban atmosphere.

The measurement of elemental composition as a function of particle size is accomplished by sampling with a cascade impactor. Plate 4 is a schematic diagram of the impactor used in connection with PIXE analysis. The basic design is that of the Battelle 5-stage impactor (Mitchell and Pilcher, 1959) and requires a flow rate of 1 liter/minute. The impactor may be

Plate 4




Source: A-8.
A.P. Woodard, Jr., B. Jensen, A.C.D. Leslie, J.W. Nelson, J.W. Winchester, R.J. Ferek, and P. Van Espen, Aerosol characterization by impactors and streaker sampling and PIXE analysis, in Proceeding of Symposium, Recent Advances in Air Pollutant Analysis, American Institute of Chemical Engineers, New York, (in press) 1977.

operated in any position so that air may be drawn vertically downward into the device from the top, or the impactor may be inverted face down so that air is drawn upward from below. The air is passed successively through a series of circular orifices of decreasing diameter which causes the linear flow rate of air to speed up as it goes through successive stages. Directly downstream of each orifice is an obstruction in the form of a sticky Mylar film backed by a solid support surface such that the largest particles passing through the orifices at each stage are caused to impact and stick to the Mylar surface. Smaller particles pass around the impaction surface but at the next stage, owing to increased air velocity, the largest of them will be collected by impaction. The impactor has been designed to give 50% collection efficiency for stages 0 through 5 of 8, 4, 2, 1, 0.5 and 0.25 μm aerodynamic diameter, so that the particle size range of the stages is the range of diameters between these values. Particles smaller than those collected by impaction stage 5 are collected by filter stage 6. The Nuclepore filter used is of small enough pore diameter to assure at least 60% collection of any particle size (Liu and Lee, 1976); calculations show that the minimum efficiency is in the range of the few hundredths of a micrometer diameter where diffusion and impaction mechanisms of particle uptake by the filter are comparable. Each sample is collected conveniently in a small area suitable for analysis by the proton beam in PIXE.

It should be emphasized that the particle size discrimination of the cascade impactor is effective for particles as small as 0.25 μm aerodynamic diameter. (Physical diameter differs from aerodynamic diameter if the density of the particles is different from 1 $g/cm^3$ and the shape of the particles is sufficiently different from spherical to cause shape-dependent air drag effects.) Cascade impactors may be designed to operate at higher flow rates but generally with the smallest size cut at larger diameters, e.g. 0.5 μm or greater. The work described in this report will demonstrate that the information obtained by small particle size resolution in the 0.25 μm range is extremely valuable for interpreting sources and transformations of trace elements in atmospheric particulate matter. Moreover, the response of the human respiratory tract to inhalation of fine particles varies significantly with particle diameter in the 0.25 μm region so that health effects can better be evaluated if particle size distribution and composition for particles this small can be determined.

The time variability of trace metal concentrations in the air can be obtained easily and automatically if sampling is carried out with a filter sampler whose exposed surface is changed continuously. In Plate 5a a diagram of a special sampler developed at Florida State University for this program is shown. This time sequence filter sampler consists of a single

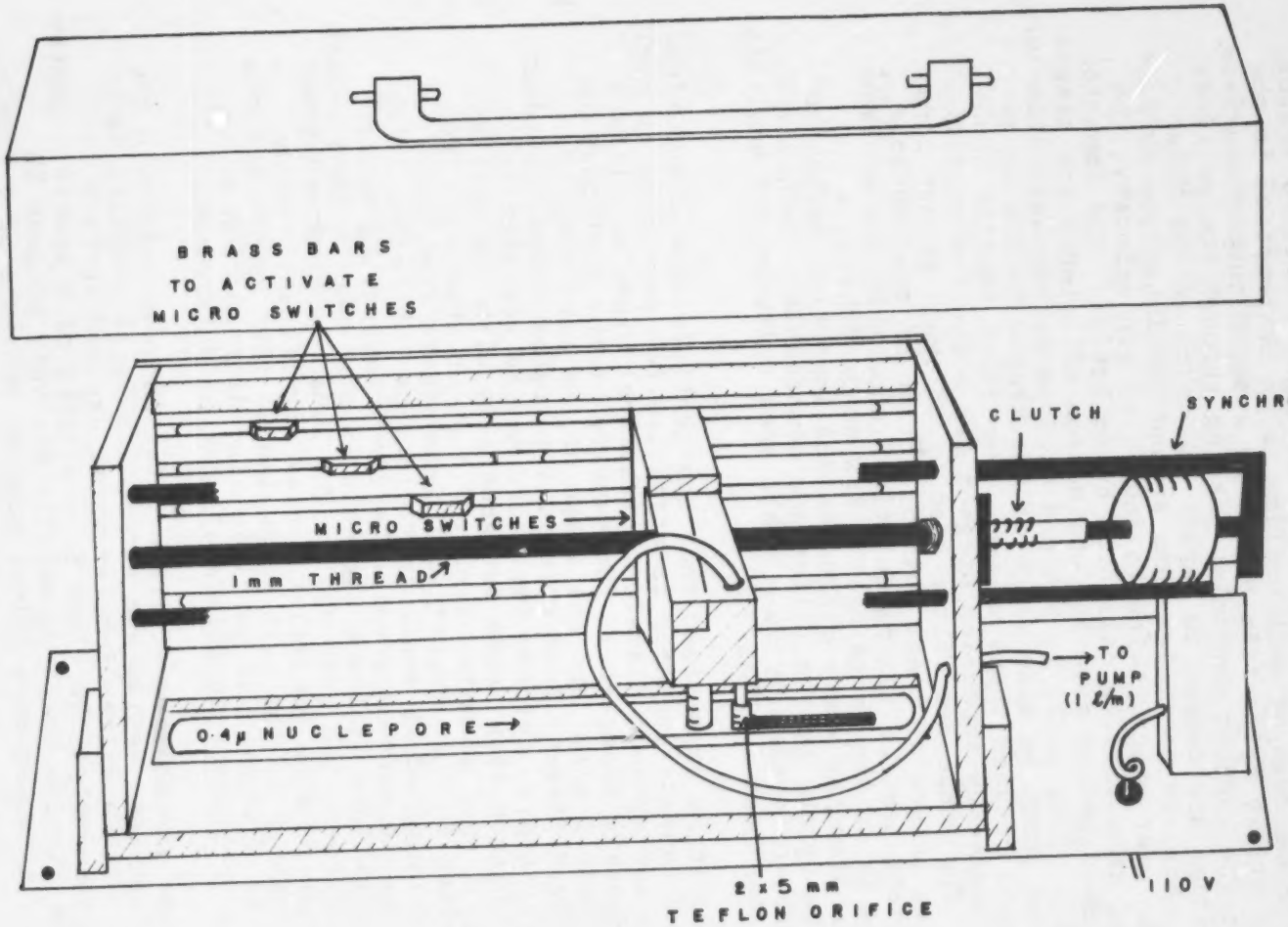



Plate 5a

Source: A-8.
A.P. Woodard, Jr., B. Jensen, A.C.D. Leslie, J.W. Nelson, J.W. Winchester, R.J. Ferek, and P. Van Espen, Aerosol characterization by impactors and streaker sampling and PIXE analysis, in Proceeding of Symposium, Recent Advances in Air Pollutant Analysis, American Institute of Chemical Engineers, New York, (in press) 1977.

Plate 5b

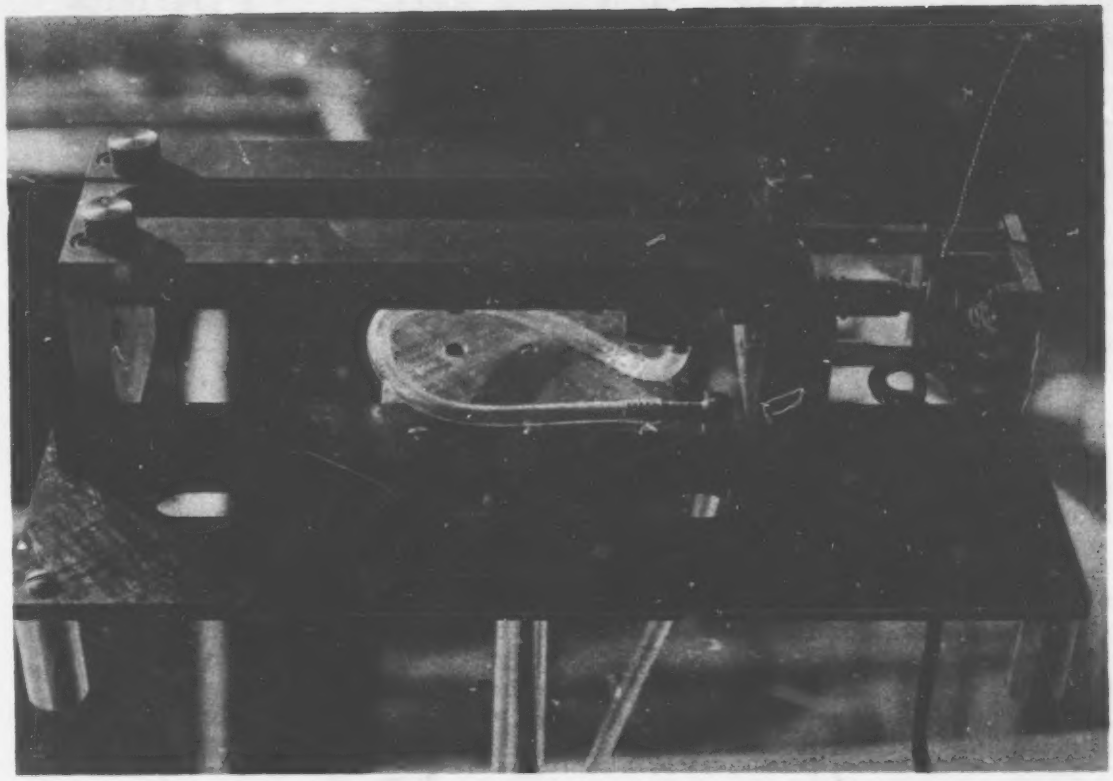


Figure 2.1 View of the continuous filter sampler. The 2- X 5- mm air intake (upper right center) is driven to the left at a rate of 1 mm per hour by the synchronous motor. A Nuclepore filter strip is placed over the intake to produce an 84- mm long strip sample in one week.

Source: B-11.
J. William Nelson, Proton-induced aerosol analyses: methods and samplers, in X-Ray Fluorescence Analysis of Environmental Samples, Thomas G. Dzubay, editor, pp. 19-34, Ann Arbor Science Publishers, 1977.

strip of Nuclepore filter stretched on a frame and mounted in a device which causes a sucking orifice on Teflon or other smooth plastic to be drawn gradually from one end of the filter to the other. The sucking orifice is attached to a vacuum pump, and as the orifice is drawn along the length of the filter, the suction seals the orifice to the smooth back of the Nuclepore while at the same time permitting air to be drawn through the filter at a rate controlled by its porosity. The device is designed to be driven by a clock motor connected to a precision threaded screw so that 7 days (168 hours) is required for a full transit along the length of the filter. In urban atmospheres a feasible streak of aerosol particle deposit is produced over the one week sampling period. Thus the sampler is known as a "streaker." If desired the clock mechanism can be used to control other sampling devices in a sampling program by means of micro-switches which are attached to the moving orifice mounting bracket. These micro-switches can be activated by small brass bars mounted in positions as desired so as to close electrical circuits at specific times. These circuits may be used to automatically operate other samplers, for instance cascade impactors, during the streaker sampling period.

The Nuclepore filter strip can be analyzed sequentially by the proton beam in time steps corresponding to sampling time intervals of two hours or less. In our accelerator bombardment facility we carry out these stepwise bombardments semi-automatically so that 90-100 separate bombardments, representing a one-week streaker scan in 2-hour time steps plus blank filter analyses, may be performed in as short a time as two hours. Although individual samples may require longer PIXE analysis times owing to low concentrations or other special considerations, the procedure does permit rapid scans of relatively large numbers of streaker samples so that data sets of many hundreds of individually analyzed time steps over a sampling network may be carried out. An illustration of the streaker sampler used in this program is shown in Plate 5b. The appearance of a typical streaker sample is shown in Plate 6 as it is being loaded into the vacuum chamber of the Van de Graaff accelerator for PIXE analysis.

Plate 6

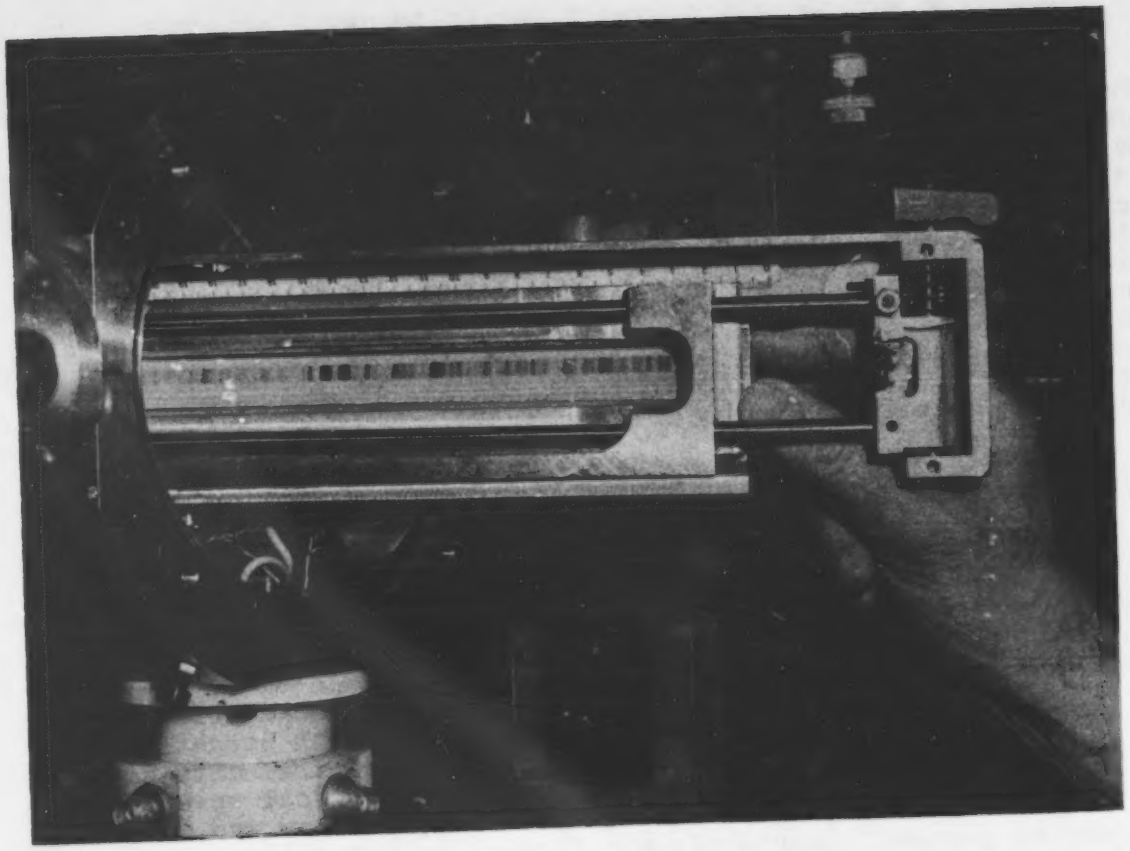


Figure 2.4 A streaker sample being inserted into the sample holding chamber in preparation for proton bombardmemt.

Source: B-11.
J. William Nelson, Proton-induced aerosol analyses: methods and samplers, in X-Ray Fluorescence Analysis of Environmental Samples, Thomas G. Dzubay, editor, pp. 19-34, Ann Arbor Science Publishers, 1977.

## SECTION 5

## CLUES TO THE SOURCES OF TRACE METALS IN URBAN AEROSOLS

Direct measurement of concentrations of trace metals in the atmosphere of a city does not in itself demonstrate the presence of air pollution. Trace metals all occur naturally as well as the result of emissions from polluting processes. In order to demonstrate the presence of a pollution component we must make use of characteristics such as particle size distribution and time and location variability of the concentrations of individual trace metals. In addition, meteorological and statistical analysis of the concentration data needs to be carried out so that associations with measures of atmospheric transport dynamics and relationships among the various trace metals may be used as clues to the kinds and locations of pollution sources which may be present.

### EVIDENCE FROM PARTICLE SIZE DISTRIBUTION

The city of St. Louis has been used as a case study area in this investigation, conducted during the Regional Air Pollution Study, RAPS. Plates 7 and 8 present the concentrations of a number of trace metals as a function of their particle size in St. Louis during August 1973. In these detailed plots most of the data points represent concentrations at an industrial area site "BH" (Broadway and Hurck Streets intersection) in the south of the city, and a central city site "HI" (Holiday Inn Downtown) during two meteorological episodes of about 2½ days each -- I during southerly air flow and II during generally northerly air flow. For comparison, additional data are shown for a north St. Louis site "WW" (Water Works), North Florida nonurban locations "NFL," and the marine atmosphere at Bermuda "BDA." For the element titanium, which has a large and distinct pollution source a short distance south of the BH site, individual samples for successive 12-hour periods beginning in the forenoon and evening of each day, August 16 to 21, 1973, are shown.

Titanium at the BH site appears to be principally derived from the pollution source when sampling was carried out during meteorological period I. During this time the generally southerly air flow transported pollution titanium over the BH sampling site and caused the concentrations to be generally in

Plate 7a

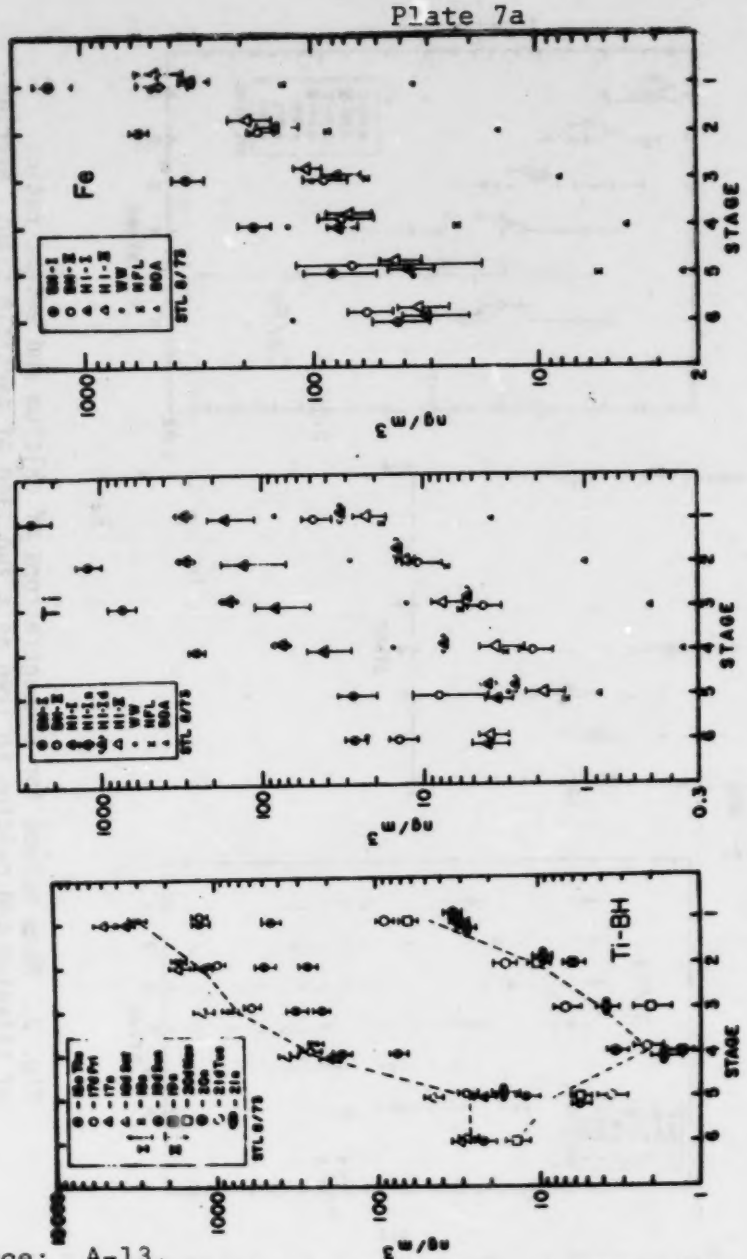



Fig. 2. Concentration of titanium and iron as a function of particle size in St. Louis aerosol, 16-22 August 1973, at BH and HI sites. Means of individual measurements for periods I and II are shown as dotted lines for Ti at BH in the left diagram. Other diagrams show means with standard deviations for periods I and II at BH and HI, with HI n and d series means also plotted separately for Ti. Averages of samples taken at locations WW, NFL, and BDA are also shown.

Source: A-13.
R. Akselsson, C. Orsini, D.L. Meinert, T.B. Johansson, R.E. Van Grieken, H.C. Kaufmann, K.R. Chapman, J.W. Nelson, and J.W. Winchester, Application of proton-induced X-ray emission analysis to the St. Louis Regional Air Pollution Study, Advances in X-Ray Analysis, vol. 18, W.L. Pickles, C.S. Barrett, J.B. Newkirk, and C.O. Ruud, eds., pp. 588-597, Plenum Press, New York, 1975.

Plate 7b

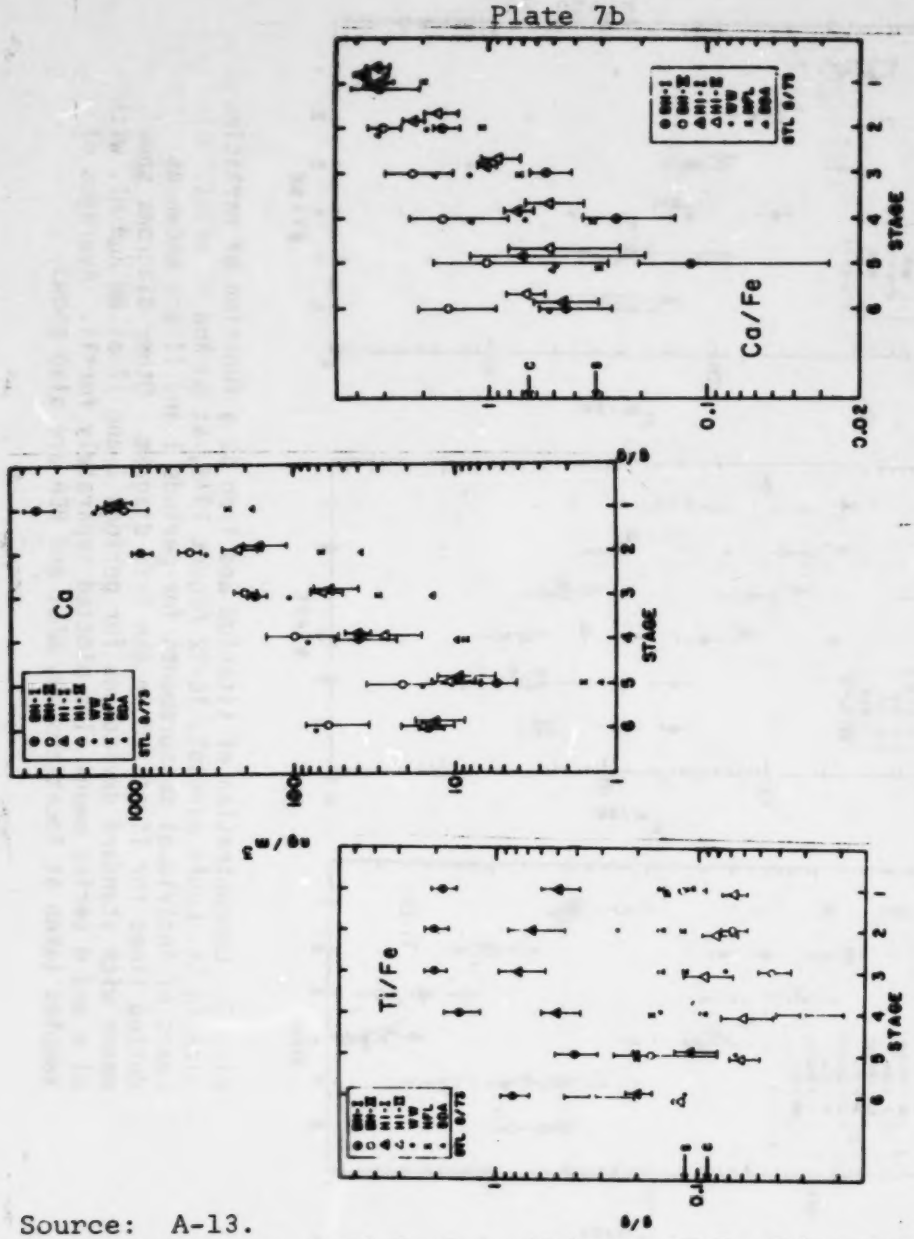



Fig. 3. Mean values for concentrations of calcium and weight ratios of titanium and calcium to iron as a function of particle size. Average composition of soil(s) and earth's crust(c) are shown for Ti/Fe and Ca/Fe. Upper limits to means are indicated by curved marks above points.

Source: A-13.
R. Akselsson, C. Orsini, D.L. Meinert, T.B. Johansson, R.E. Van Grieken, H.C. Kaufmann, K.R. Chapman, J.W. Nelson, and J.W. Winchester, Application of proton-induced X-ray emission analysis to the St. Louis Regional Air Pollution Study, Advances in X-Ray Analysis, vol. 18, W.L. Pickles, C.S. Barrett, J.B. Newkirk, and C.O. Ruud, eds., pp. 588-597, Plenum Press, New York, 1975.

Plate 8a

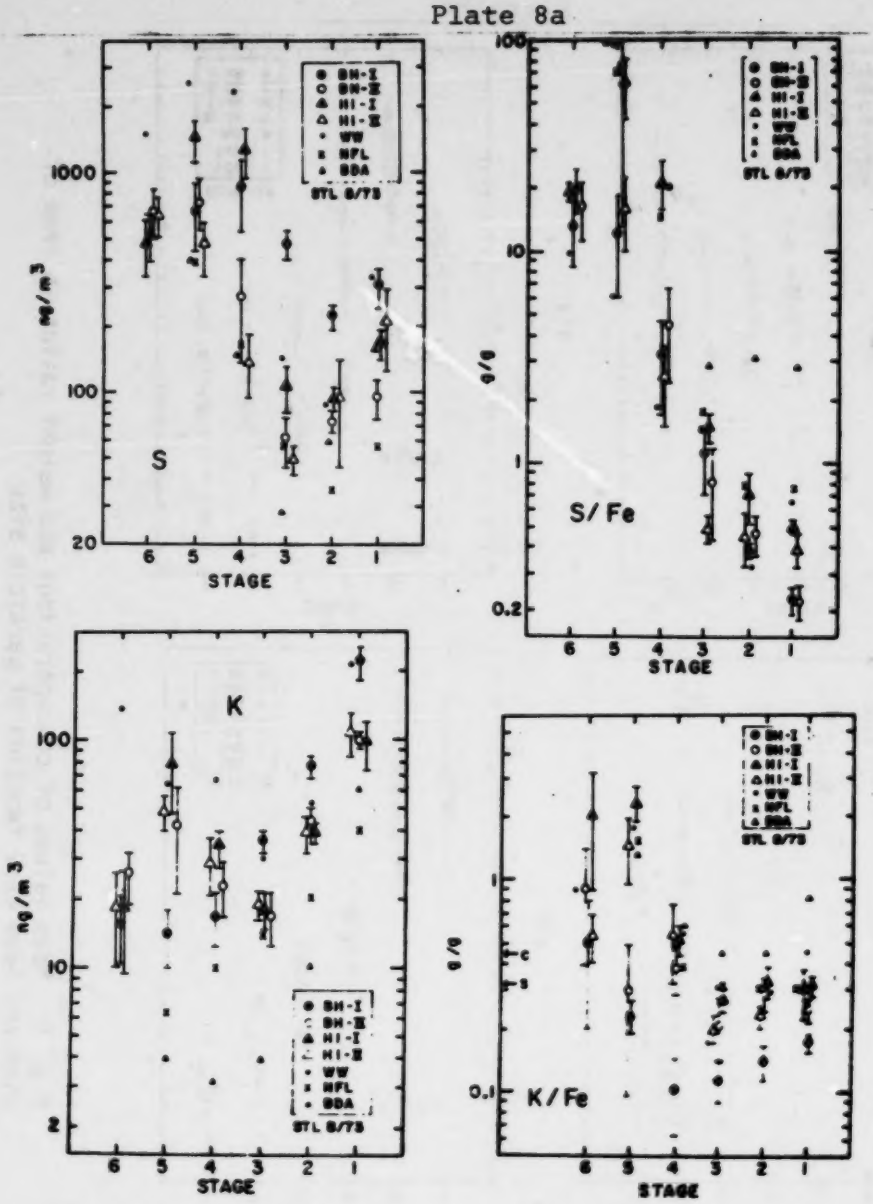



Fig. 4. Mean values for concentrations and weight ratios to iron of sulfur and potassium as a function of particle size.

Source: A-13.
R. Akselsson, C. Orsini, D.L. Meinert, T.B. Johansson, R.E. Van Grieken, H.C. Kaufmann, K.R. Chapman, J.W. Nelson, and J.W. Winchester, Application of proton-induced X-ray emission analysis to the St. Louis Regional Air Pollution Study, Advances in X-Ray Analysis, vol. 18, W.L. Pickles, C.S. Barrett, J.B. Newkirk, and C.O. Ruud, eds., pp. 588-597, Plenum Press, New York, 1975.

Plate 8b

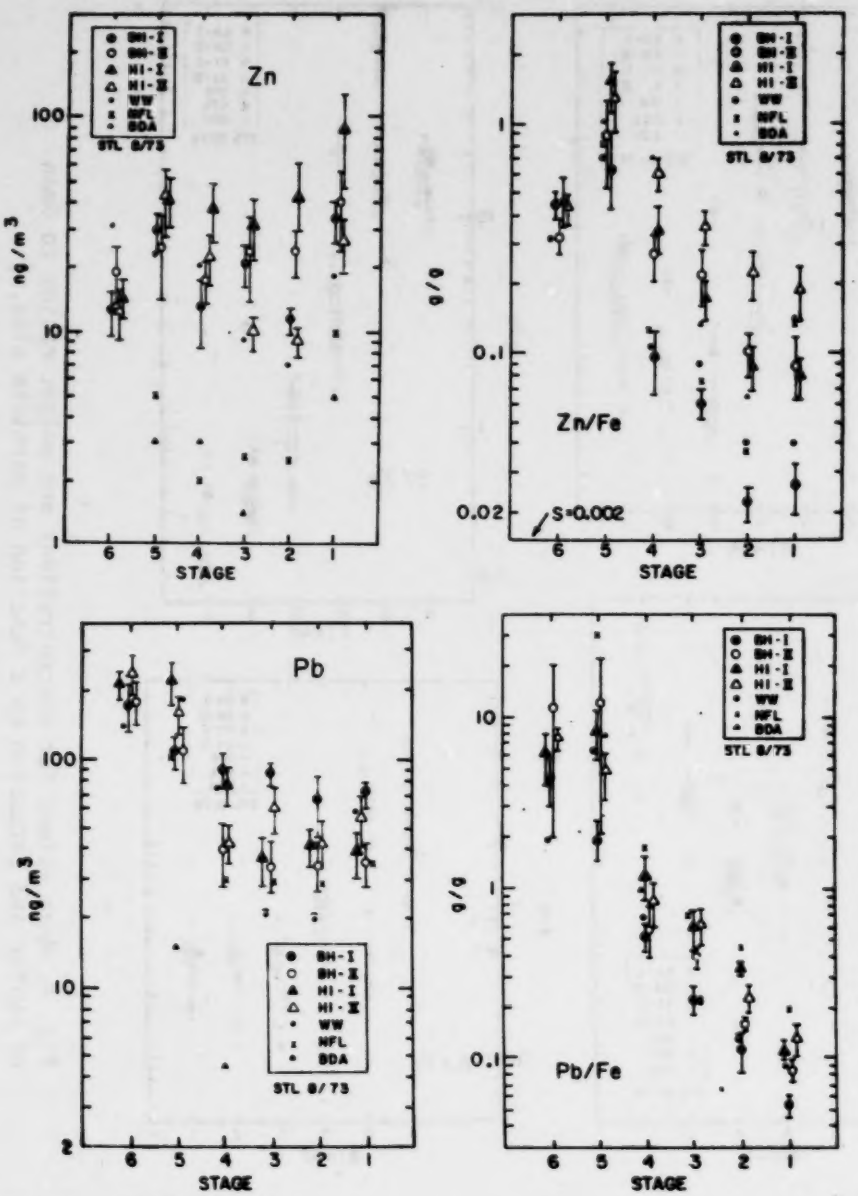



Fig. 5. Mean values of concentrations and weight ratios to iron of zinc and lead as a function of particle size.

Source: A-13.
R. Akselsson, C. Orsini, D.L. Meinert, T.B. Johansson, R.E. Van Grieken, H.C. Kaufmann, K.R. Chapman, J.W. Nelson, and J.W. Winchester, Application of proton-induced X-ray emission analysis to the St. Louis Regional Air Pollution Study, Advances in X-Ray Analysis, vol. 18, W.L. Pickles, C.S. Barrett, J.B. Newkirk, and C.O. Ruud, eds., pp. 588-597, Plenum Press, New York, 1975.

the range of 1,000 ng/$m^3$ or above. Particle sizes containing most of the titanium were greater than 1 μm aerodynamic diameter, i.e., impactor stages 3, 2, and 1. During meteorological period II, generally northerly air flow, the titanium concentrations decreased to 100 ng/$m^3$ or less and were principally found in particles of diameter greater than 4 μm, impactor stage 1. The latter values may represent a mixture of natural dust and other pollution titanium, e.g. from fly ash, whereas the former represent primarily contributions from the unique titanium pollution source. This source, which emitted $TiO_2$ particles from a paint manufacturing process, apparently added smaller sized particles to the atmosphere than did the other dust sources.

At the HI site it was found that the alternating 12-hour sampling during meteorological period I showed more than 10 times higher concentrations during the AM ("n," night and morning) than the PM samples ("d," afternoon and evening). The former high concentrations we attribute to fumigation of an overlying polluted layer during early morning break-up of an atmospheric temperature inversion. This interesting case of vertical pollution transport in the atmosphere of St. Louis is discussed further below.

The particle size distribution of iron in the St. Louis samples is shown in Plate 7. At the HI site concentrations are not strictly dependent on wind direction as indicated by similarity between meteorological periods I and II. During period I at the BH site iron concentrations were higher, but during period II they were similar to those found at HI. Iron is known to be emitted by steel mills and other sources in the urban area of St. Louis. No single unique source for iron is identified as is the case for titanium. However, one of the pollution sources may be locally very important in the south St. Louis industrial region and account for the high BH values during period I.

It is significant that iron in the smaller particle size fractions, <1 μm diameter, stages 4, 5, and 6, is found at relatively much higher concentrations than is found in the North Florida aerosol, NFL, or the presumably terrestrially derived iron at Bermuda, BDA. The coarse particle iron concentrations in St. Louis are generally only somewhat higher than in the relatively clean North Florida atmosphere; however, the fine particle iron appears to be present in much greater abundance. This result suggests that the impact of polluting activities on the content of iron in the atmosphere of St. Louis is greatest in the sub-micrometer respirable size range.

Plate 7 includes a plot of the ratio Ti/Fe for the different sampling locations and periods. In clean atmospheres, as exemplified by North Florida and Bermuda, the ratio Ti/Fe is very close to 0.1, the average composition of soil and the

earth's crust. During the northerly air flow period II in St. Louis, the ratio is significantly below this value suggesting the presence of additional iron, such as from steel mills, which does not contain relatively as much titanium as average earth crust materials. The depression of Ti/Fe below 0.1 is more pronounced for sub-micrometer particles than for larger sizes, in keeping with our observation earlier that the pollution impact on iron concentrations was greater for smaller particle sizes. Also shown in this figure are the very much higher Ti/Fe ratios, often in excess of unity, when the localized titanium pollution source made its greatest contribution. The particle size distribution of Ti/Fe indicates that the pollution titanium is present in larger particles on the average than is the case for pollution iron, although both elements' pollution contribution may be mainly in smaller particle sizes than that of soil dust.

In Plate 8 the particle size distributions of zinc and lead contrast significantly from those of iron. Both elements are enriched strongly above earth's crust values relative to iron, and zinc to a greater degree than is seen in North Florida, which suggests that pollution sources predominate over natural sources in St. Louis. Both elements are found to a much greater extent on smaller particle sizes in the sub-micrometer respirable range than is the case for iron. These results suggest the importance of pollution emissions at high temperatures, which may favor the formation of smaller particle sizes and more efficient transfer to the atmosphere through stack emission control devices than would be the case for more refractory and coarse particulate ash. Sulfur likewise shows a tendency to be found on smaller particle sizes, although a secondary mode of sulfur is found on coarse particles. The elements potassium and calcium contrast with each other, in that potassium appears to have a greater abundance in fine particles relative to coarse than is the case for iron, whereas the particle size distributions of calcium and iron are similar. These results suggest that some potassium may enter the atmosphere with combustion gases or fine particles formed from them, whereas calcium may be essentially nonvolatile even at high temperatures.

From these particle size distributions we have been able to formulate lines of further inquiry concerning possible sources of these trace metals in the atmosphere of St. Louis. The ideas presented for possible sources should be used as the basis for more detailed investigation and verification of the hypotheses stated.

Plate 9 is a more detailed presentation of the time variability of titanium and other elements at station HI mentioned above. We have plotted, as a function of time every 12 hours from August 17 to 22, 1973, the concentrations of

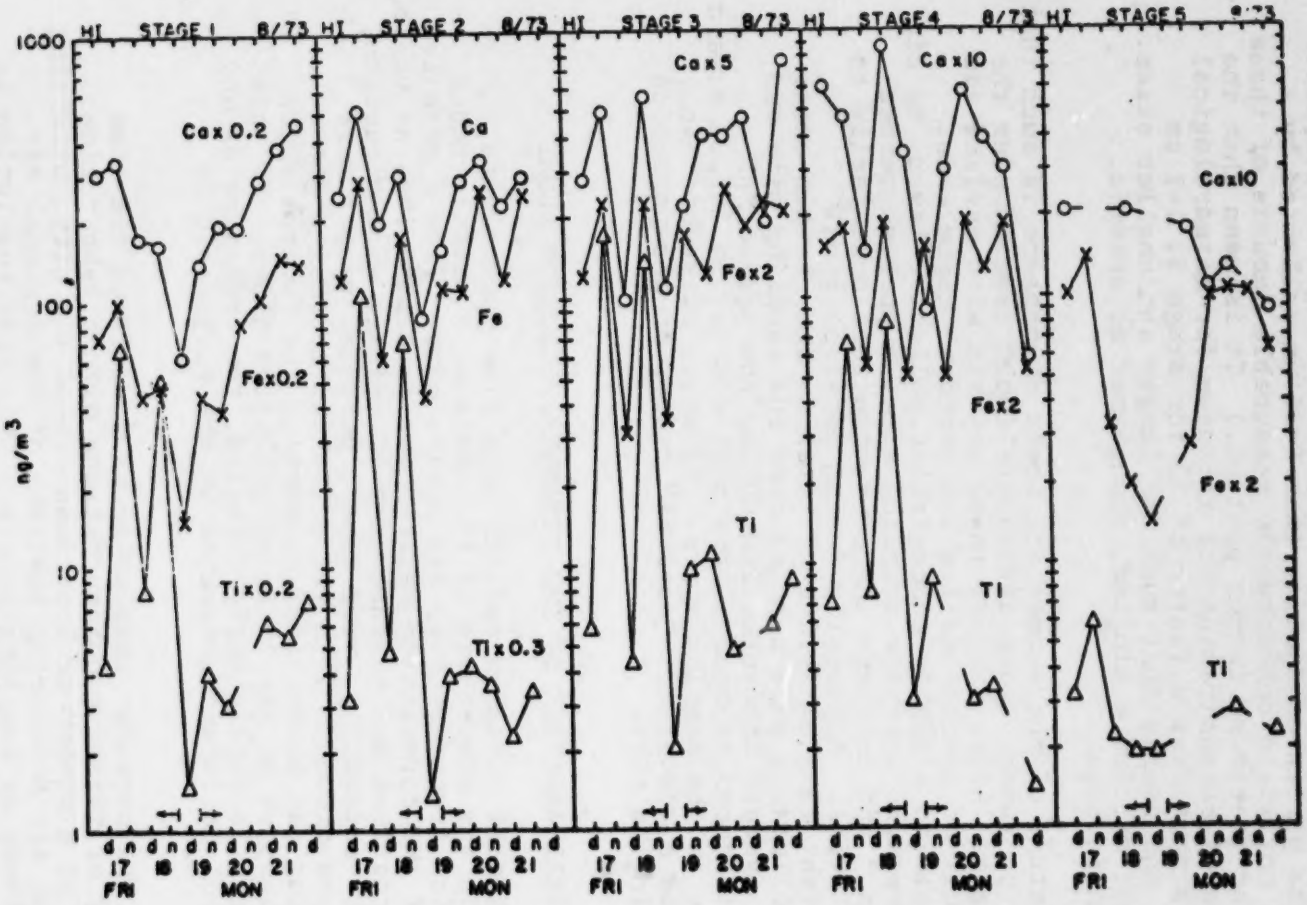



Fig. 2a. Concentrations of calcium, iron, and titanium as a function of sample collection time at Holiday Inn Downtown, St. Louis, 17-22 August, 1973.

Source: A-12.
John W. Winchester, Dennis L. Meinert, J. William Nelson, Thomas B. Johansson, Rene E. Van Grieken, Celso Orsini, Henry C. Kaufmann, and Roland Akselsson, Trace metals in the St. Louis aerosol, Proceedings of the Second International Conference on Nuclear Methods in Environmental Research, July 29-31, 1974, University of Missouri, Columbia, J.R. Vogt and W. Meyer, eds., USERDA CONF-740701, pp. 385-394, 1974.

titanium, iron and calcium for each individual particle size fraction collected by impactor stages 1 through 5. (Impactor stage 6, the particles smaller than 0.25 μm collected by a filter did not yield consistently measurable amounts of these elements and therefore is not plotted.) It is seen that the alternation of concentration for titanium for meteorological period I extends over a factor of 30 for stage 3, 1-2 μm particles, and nearly that much for larger and smaller sizes. For iron and calcium a similar, though not as drastic, alternation is seen.

The nature of the summer St. Louis atmosphere is such that stratified pollutant laden air layers could develop over the city at night. After sunrise these may mix with surface air as the result of ground heating and vertical turbulence. This may lead to a highly concentrated pollution layer, to dip suddenly downward over the sampling site, a process termed "fumigation," and increase the concentrations momentarily to very high levels. Apparently during meteorological period I night time emissions of titanium and certain other metallic pollutants were carried over the sampling site and caused the average concentration during the period "n" (midnight to noon) to become very high due to the influx toward the surface in the morning hours. Titanium therefore has proved to be a convenient "natural" tracer of air-pollution transport in the city.

## METEOROLOGICAL ANALYSIS OF THE TITANIUM POLLUTION PLUME

The element titanium emitted as a fine particluate pollutant in the atmosphere of St. Louis is a useful tracer for pollution transport over the entire city. From a detailed analysis of the correlation between its concentrations at various sampling locations and measurements of average wind direction, directional variability, wind speed, vertical temperature gradient, and distance from the pollution source, a good understanding can be obtained concerning the factors which control transport of the titanium pollution plume. If this understanding is sufficiently detailed, the transport of any other aerosol pollutant generated in the city could be predicted.

Using the streaker sampler we have measured the time variability of titanium concentrations with a 2-hour time resolution at a number of locations around the city, utilizing the Regional Air Monitoring Stations of the Regional Air Pollution Study as sampling points. This time resolution is comparable to that of the meteorological parameters obtained at these stations.

Plate 10 shows as examples the trend of titanium concentration seen at two of the Regional Air Monitoring Stations. Station 105, located 11 kilometers to the NNE of the titanium pollution sources across the Mississippi River in Illinois, shows concentrations reaching almost 1,500 ng/$m^3$ although most of the time the concentrations are only a few tens of ng/$m^3$. At station 122 some 60 kilometers to the north in Illinois, the titanium fluctuations are also seen although the peak values are 10 times lower. At other stations similar fine structure to the titanium time variability is observed. The sharp maxima seen over short intervals of time are presumed to represent transport of the titanium pollution plume on the sampling site.

It would be useful to know if the plume transport can be understood in terms of routinely measured meteorological variables. If so, we could develop an ability to forecast pollution transport of any trace metal in plumes. Four stations were selected for a meteorological analysis of the time variability of titanium. These stations are arranged in a line generally running from the titanium source northward and at a distance of 5, 11, 21 and 35 kilometers for stations 111, 105, 113 and 121 respectively. Since the titanium pollutant is emitted from stacks which are about 35 m in altitude, whereas the samplers were placed at about 10 m height, both vertical and horizontal transport must occur for the titanium to reach the sampler.

The meteorological analysis employed consisted of first sectoring the concentrations measured over the one-week study period into groups according to the local wind direction observed at each sampling station. The sectoring scheme differed somewhat among the four stations so as to provide a suitable number of observations within each sector for the statistical analysis. These sectoring schemes are shown on Plate 11.

Treating the observations within each sector as individual subsets, it was generally found that concentrations were highest in the directly downwind sector (5 for stations 111 and 105 and 4 for stations 113 and 121). However, the concentrations were not uniformly high in these sectors and sometimes high concentrations were observed for the nearby wind direction sectors. Therefore interactions between the sectors and the meteorological measurements of standard deviation of wind direction (i.e., directional variability), wind speed, and the temperature differences between 30 m and 5 m (a measure of temperature gradient) were examined. In Plate 11 a summary of these correlations is presented. The sign, positive or negative, of the parameter b indicates qualitatively whether the correlation is direct or inverse.

Plate 10

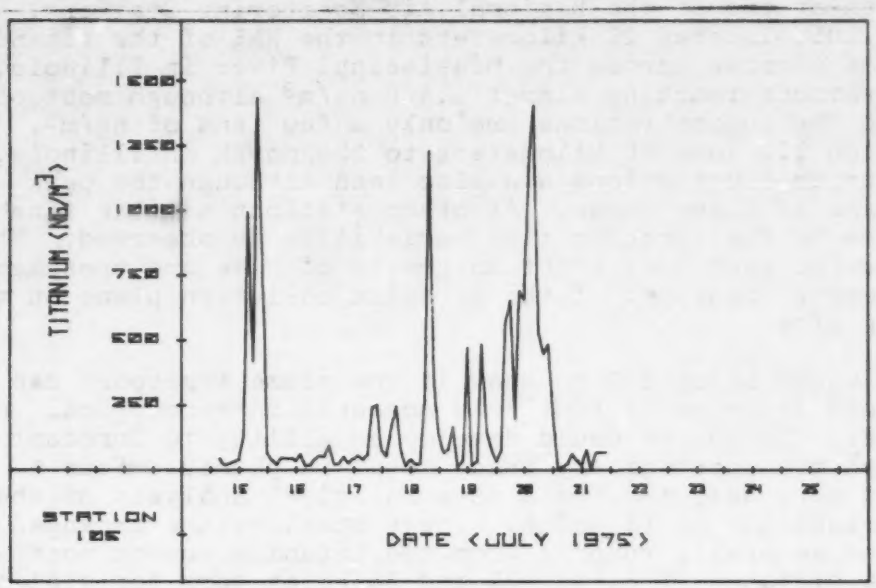



Fig. 6. Titanium versus time at station 105.

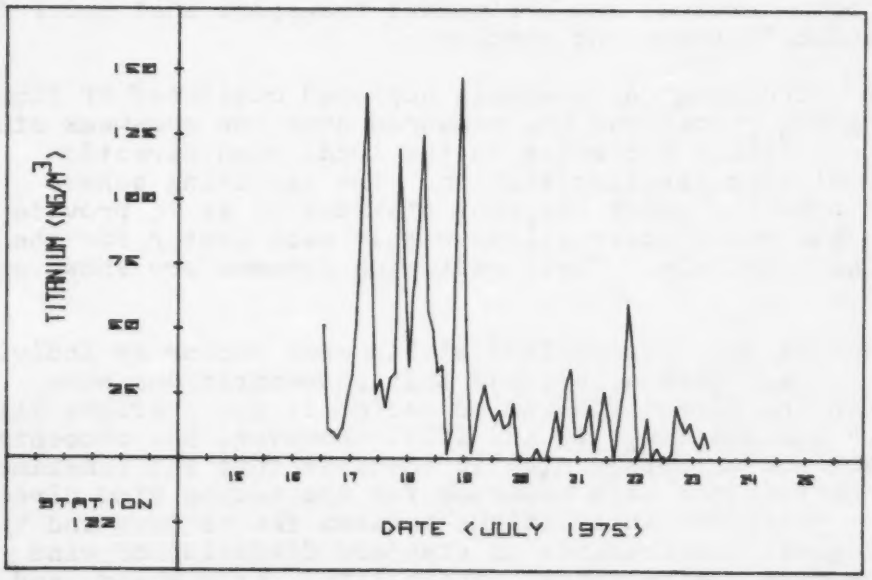



Fig. 9. Titanium versus time at station 122.

Source: D-2.
Scott Rheingrover, A Statistical Model for Titanium Pollution Transport in the Atmosphere of St. Louis, M.S. Thesis, Dept. of Meteorology, Florida State University, June 1977.

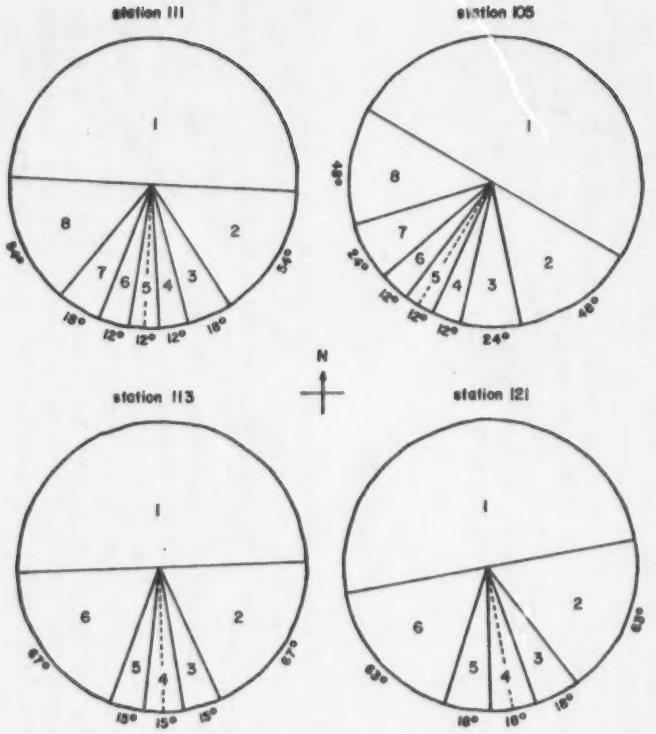



Fig. 10. Sectoring schemes for stations 111, 105, 113, and 121 with the theoretical source to station plume centerline angle represented by the dashed line, the sectors numbered clockwise starting with the 180 degree upwind sector numbered 1, and the degree width of the remaining downwind sectors labled on the perimeter.

TABLE IX. Final form of the Interaction Dummy Variable Multiple Regression Model

| Station 111 | | | Station 105 | | |
|---|---|---|---|---|---|
| Variable | b | sig | Variable | b | sig |
| SECTOR3 | +1.86 | .000 | SECTOR3 | +1.96 | .000 |
| S3BYSPD | -0.45 | .006 | S3BYSTD | -0.05 | .008 |
| SECTOR4 | +4.54 | .001 | S3BYGRAD | -0.77 | .002 |
| S4BYSPD | -0.85 | .014 | SECTOR4 | +5.06 | .009 |
| S4BYGRAD | -0.75 | .105 | S4BYSPD | -0.35 | .089 |
| SECTOR5 | +2.12 | .000 | S4BYSTD | -0.05 | .035 |
| S5BYSTD | -0.03 | .055 | S4BYGRAD | -1.70 | .023 |
| SECTOR6 | +4.70 | .023 | SECTOR5 | +0.99 | .000 |
| S6BYSTD | +0.06 | .111 | SECTOR7 | +1.43 | .052 |
| S6BYGRAD | -2.39 | .046 | S7BYSPD | -0.25 | .150 |
| S7BYSTD | +0.05 | .000 | Constant | +1.69 | .000 |
| Constant | +1.55 | .000 | | | |
| | $R^2$ = .721 | | | $R^2$ = .487 | |

| Station 113 | | | Station 121 | | |
|---|---|---|---|---|---|
| Variable | b | sig | Variable | b | sig |
| SECTOR3 | +1.46 | .001 | S4BYSPD | +0.18 | .000 |
| S3BYSPD | -0.12 | .111 | S4BYSTD | -0.06 | .000 |
| SECTOR4 | +56.73 | .012 | S4BYGRAD | +0.85 | .000 |
| S4BYSPD | -3.48 | .009 | SECTOR5 | -1.04 | .075 |
| S4BYSTD | -0.08 | .001 | S5BYSPD | +0.26 | .006 |
| S4BYGRAD | -20.96 | .017 | S5BYGRAD | +0.40 | .069 |
| Constant | +1.64 | .000 | Constant | +1.55 | .000 |
| | $R^2$ = .797 | | | $R^2$ = .903 | |

Source: D-2.
Scott Rheingrover, A Statistical Model for Titanium Pollution Transport in the Atmosphere of St. Louis, M.S. Thesis, Dept. of Meteorology, Florida State University, June 1977.

Plate 11

The calculations indicate that variability in wind direction is associated with higher concentrations of titanium in sectors adjacent to the directly downwind sector, implying horizontal dispersion during plume travel. However, the reverse is found for the directly downwind sector, suggesting plume dilution during variable winds which reduces concentrations. Higher wind speeds tend to be associated with lower concentrations at nearby stations suggesting turbulent mixing, but at more distant stations wind speed is associated with higher concentrations suggesting the importance of less time available for particle settling en route. The temperature gradient information indicates that vertical mixing downward enhances concentration at nearby stations but enhances removal and lowers concentrations by the time the plume reaches more distant stations. The overall variability accounted for by the statistical analysis is 70-90% for three of the stations but is less for station 105. This station is separated from the titanium source by the waters of the Mississippi River, compared with the other stations where plume transport occurs only over land. The perturbing effect of the water thus could account for greater variability observed for station 105 than is seen for the other three stations. However, the overall degree of variability at the four stations accounted for by this analysis is impressive.

In Plate 12 a schematic diagram is presented for the apparent plume movements for both vertical and horizontal directions for the four stations downwind of the titanium source. The diagram, which has been constructed purely on the basis of the statistical analysis, is in good agreement with conventional ideas concerning plume transport. The titanium "natural" tracer is thus a means of quantifying the description of a plume as it is transported over a complex urban area. The quantitative calibration of a plume model may permit prediction of the transport of any plume carrying pollutants across the city.

## LEAD, A MULTIPLE SOURCE POLLUTANT IN ST. LOUIS

Conventional wisdom says that urban lead is predominantly derived from the combustion of leaded gasoline. The attention given to this idea by air pollution investigators has tended to obscure the fact that lead in the urban atmosphere may be derived from other pollution sources as well. In the city of St. Louis other potential lead aerosol sources include the smelting of ores, the combustion of fuels, and metallurgical refining processes. The contributions of these sources to the overall atmospheric inventory of lead in St. Louis must be determined before we can accurately predict the adequacy of different emission control strategies on air quality.

Plate 12

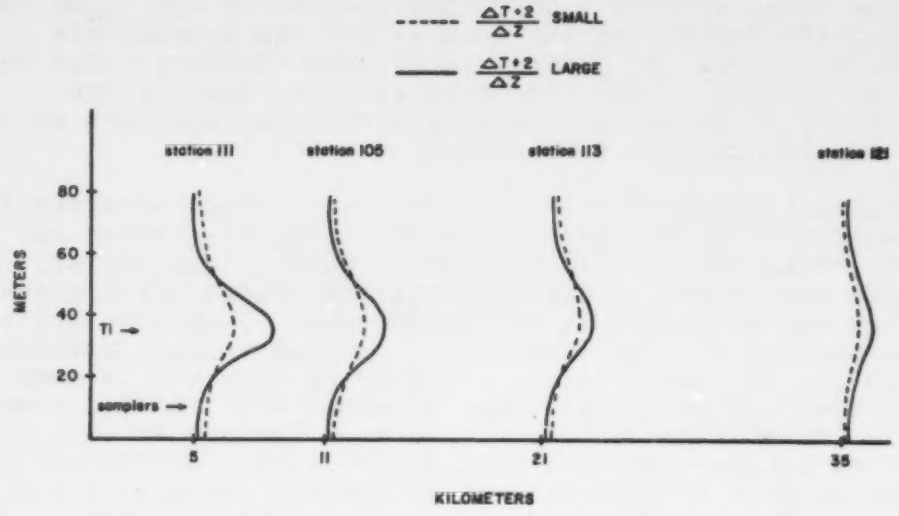



Fig. 18. Vertical (XZ) plume concentration profiles suggested by the $\frac{\Delta T+2}{\Delta Z}$ associations. (Adapted from Strom, 1976)

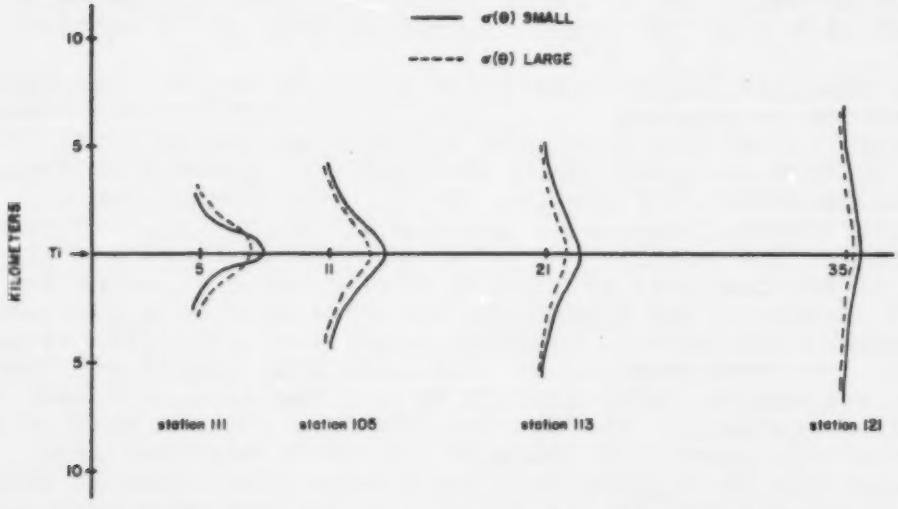



Fig. 17. Horizontal (XY) plume concentration profiles suggested by the σ(θ) associations.

Source: D-2.
Scott Rheingrover, A Statistical Model for Titanium Pollution Transport in the Atmosphere of St. Louis, M.S. Thesis, Dept. of Meteorology, Florida State University, June 1977.

The time sequence filter sampler has a capability for collecting a large enough number of samples at many sites around the city so that a data set of sufficient size for statistical analysis may be assembled in a reasonable length of time. To test the possibility of resolving lead into its different components, a weeklong record of lead concentration was obtained with 2-hour time resolution for 11 of the Regional Air Monitoring Stations within and immediately outside the city. In general 10 or more elements could be detected in each of the time step samples, opening the possibility of using correlations with other elements as the basis for identifying different sources of lead.

Plate 13 shows a detail of the time trends observed for a one-day period, Thursday, July 17, 1975, at station 111 in an industrial section of St. Louis. During this day all elements were found to exhibit large concentration fluctuations, although not at precisely the same times. Thus iron and zinc show a maximum at time step 14 but calcium shows a maximum at step 15, two hours later. Of special interest is lead which shows a step 14 maximum. Bromine, with which automotive lead is invariabily associated, shows a maximum at step 13, two hours earlier than the maximum for lead. Similarly the earlier maximum of lead at step 9, corresponding to a zinc maximum at step 9, does not correspond to the maximum of iron at step 8 or that of bromine, also at step 8. Unless automotive lead and bromine can become decoupled in the atmosphere to such an extent as to cause these time shifts, the data suggest that lead has other sources as well as automotive.

A multiple linear regression analysis of lead has been carried out to examine the extent of correlation with other elements, in which each of the elements of the data set is taken in turn as independent variables. A summary of the results is shown in Plate 14. At all stations in the 11 station network, bromine is the element most highly correlated with lead. Its coefficient of about 5 is in keeping with the ratio of bromine/lead of about 0.2 often seen in urban environments. However, the regression analysis continues by examining the correlation between residual lead, i.e., the difference between the lead measured in each time step sample and the smooth regression curve through all of the data, and each of the other elements. At 7 of the stations zinc is seen to be a significantly correlated element with this residual lead. The coefficients suggest that the zinc-related lead is about 1/10 as abundant as the apparently automotive bromine-related lead. The zinc-related lead could be derived from the smelting of lead zinc ores.

As the regression analysis is continued, residuals of lead over and above the first two smooth regression relationships exhibit frequent correlations with other elements, including

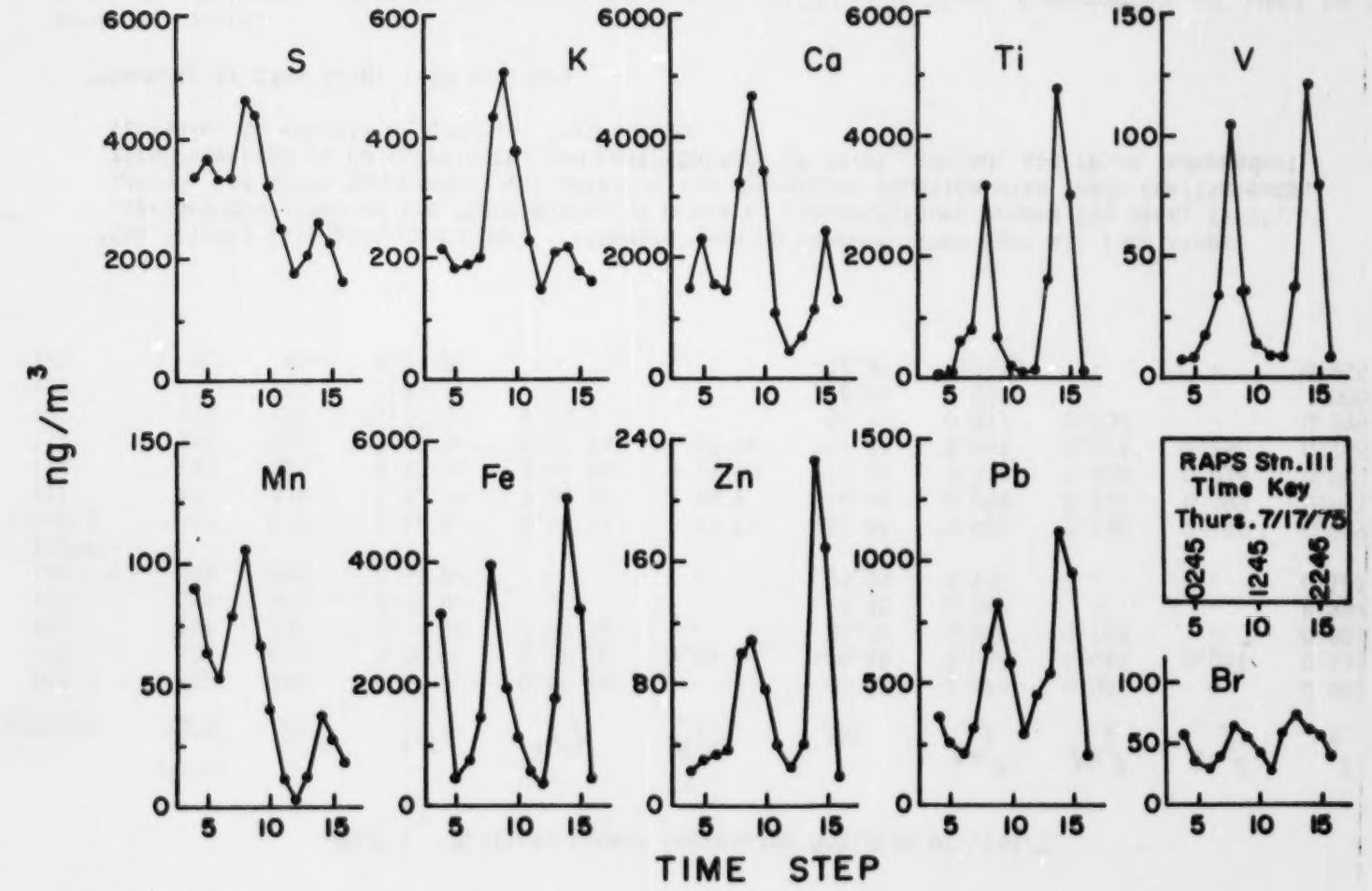



Plate 13

Source: A-16.
James O. Pilotte, John W. Winchester, and J. William Nelson, Components of lead in the atmosphere of St. Louis, Missouri, J. Applied Meteorology, 17, 627-635, 1978.

TABLE 5. Multiple Linear Regression Analysis of Lead.*

| Station | Pb av ng/m$^3$ | Pb | $a_1x_1$ | $a_2x_2$ | $a_3x_3$ | Int | $\Delta R_1^2$ | $\Delta R_2^2$ | $\Delta R_3^2$ | $R^2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 102 | 442 | 287 | 5.52 Br | 0.64 Zn | - | 41.28 | 0.978 | 0.003 | - | 0.981 |
| 104 | 640 | 436 | 5.35 Br | 0.32 Zn | 0.40 K | -64.48 | 0.862 | 0.055 | 0.034 | 0.951 |
| 105 | 464 | 330 | 4.76 Br | 1.09 Zn | - | 91.76 | 0.692 | 0.189 | - | 0.881 |
| 106 | 628 | 428 | 6.40 Br | - | - | 9.45 | 0.987 | - | - | 0.987 |
| 108 | 504 | 844 | 8.04 Br | - | - | -35.03 | 0.107 | - | - | 0.107 |
| 108** | | | | | | | | | | |
| (31-81) | 307 | 223 | 7.59 Br | 0.72 Zn | 1.33 Ti | -57.44 | 0.481 | 0.260 | 0.146 | 0.887 |
| 111 | 478 | 336 | 4.37 Br | 2.34 Zn | 2.48 V | -18.09 | 0.658 | 0.241 | 0.092 | 0.991 |
| 113 | 540 | 361 | 6.15 Br | 0.41 Zn | 0.14 Fe | 113.27 | 0.878 | 0.028 | 0.074 | 0.980 |
| 121 | 381 | 501 | 7.22 Br | 0.67 Zn | 0.67 Fe | 191.24 | 0.441 | 0.074 | 0.250 | 0.765 |
| 122 | 133 | 142 | 11.79 Br | 0.84 K | - | -86.72 | 0.917 | 0.032 | - | 0.949 |
| 123 | 115 | 108 | 7.69 Br | - | - | -16.64 | 1.000 | - | - | 1.000 |
| 125 | 82 | 63 | 6.51 Br | - | - | -12.92 | 0.9555 | - | - | 0.955 |

*The columns list station number, arithmetic mean Pb concentration over all time steps, standard deviation of the distribution of measured concentrations around the mean, first, second, and third independent variables in the regression equation with their coefficients, zero intercept on Pb coordinate, and contributions of first, second, and third independent variables to overall $R^2$ given in last column.

**Anomaly of time steps 1-30 excluded.

Source: A-16.
James O. Pilotte, John W. Winchester, and J. William Nelson, Components of lead in the atmosphere of St. Louis, Missouri, J. Applied Meteorology, 17, 627-635, 1978.

potassium and iron, which may be typical of fly ash or other earth crust materials. Such a correlation may be expected if combustion of coal is a significant contributor of lead to the St. Louis atmosphere.

Station 108 is anomalous in showing little correlation with any element other than bromine, and in fact the bromine correlation is poor. During the first 30 time steps (60 hours), lead concentrations were singularly high, although concentrations of other elements were not especially high. When the regression analysis was repeated for the following steps only, a regression result similar to many of the other stations was obtained. The anomalously high lead concentrations were subsequently found to be due to emissions from a secondary lead smelter which did not carry other associated elements into the atmosphere. Thus a new fourth atmospheric lead component in St. Louis was identified at this station.

Examining the values of $R^2$ in the last column and the partial $\Delta R^2$ values of the first, second and third regression results in the previous columns shows that on the whole a very high degree of variability in lead is accounted for. In the most nonurban stations the bromine correlation is found to account for nearly all of the variability. In such nonurban areas automotive emissions predominate over industrial sources of lead. In contrast, in the more urban locations the bromine correlation usually accounts for less of the overall variability of lead, and additional elemental correlations are found in general to account for most of the rest. Even for station 108 this is true during times when the secondary lead smelter emissions did not blow toward the sampling site.

By carrying out a multiple linear regression analysis a trace element fingerprinting of the lead from different sources has been obtained. If this result is compared with the transport modeling result of the titanium plume study described above, we see that it may also be possible to trace the transport of lead plumes across the city. Thus the complexity of the atmospheric trace metal content of the city of St. Louis may be unraveled and understood by judicious choice of sampling methods and data analysis techniques.

## SECTION 6

## AEROSOL PROPERTIES AND HUMAN RESPIRATORY EXPOSURE

Much of the interest in trace metals contained in the suspended particulate matter of the urban atmosphere stems from the potential for transfer of toxic materials to the human respiratory tract. We have already stressed the importance of particle size as providing clues about the sources of airborne trace metal pollutants in the city. The particle size is also critically important in regulating the transfer of trace metals to different parts of the human respiratory tract.

### RESPIRATORY RESPONSE IN AEROSOL INHALATION

When aerosol particles are inhaled, two distinct responses may occur: the first is the effect of the high humidity of the respiratory tract on the incoming particles, possibly causing a sudden particle size increase if the inhaled air is initially dry and if the particles themselves are hygroscopic. The second is the deposition of incoming aerosol particles in different parts of the respiratory tract, with an efficiency which depends on particle size after humidification. The largest particles tend to be removed from the inhaled air by impaction in the nasal passages and the ciliated regions of the upper respiratory tract. However, particles smaller than about 1 μm diameter may bypass these regions and enter the pulmonary region. There they may be deposited on the lung walls, but some particles are not deposited and may be exhaled again. Particles that are substantially smaller than 0.25 μm are deposited by their Brownian diffusion to the walls of the pulmonary sacs and retained in the lung; the efficiency of deposition by diffusion increases with decreasing particle size. Therefore viewing the lung as a whole the largest particles and the smallest particles may be scavenged from the inhaled air in the upper and the lower regions, respectively, by these two mechanisms, but intermediate sized particles, in the region of a few tenths of a micrometer diameter, may be retained by the lung to a lesser extent and exhaled with the next breath. Thus the efficiency of particle deposition in the respiratory tract exhibits a minimum in the 0.5 μm size range. To determine the position of the minimum experimentally for a specific aerosol

type requires that the effect of humidification be clearly distinguished from the effect of deposition so that the effective size of the particles within the lung can be determined.

The PIXE technique is sufficiently sensitive so that a human being breathing normally polluted air for a matter of minutes into a cascade impactor can exhale enough trace metal to be collected by the impactor stages and be detected by PIXE. This makes it practical to measure simultaneously the concentrations of trace metals in particle size fractions collected by identical cascade impactors sampling the ambient atmosphere and the exhaled human breath. The ambient atmosphere should preferably be brought to a high relative humidity corresponding to that in the lung before the sampling.

On Plate 15 the results of an experiment are shown comparing the particle size distributions of 8 elements in welding fume aerosol sampled in the unhumidified inhaled air and the humidified exhaled air. The prominent feature is a twofold increase in average particle diameter owing to the humidification effect. In addition, careful numerical analysis of 9 similar tests shows that particle deposition in the respiratory tract also occurred to the extent of 20 to 50% depending on the element. The lower part of Plate 15 shows the results of another of the 9 tests, this being an anomalous run in which the particle size shift was not observed. The anomaly is probably associated with a slight temperature difference between the exhaled breath temperature and that at which the cascade impactor was maintained, which would cause a difference in relative humidity in the sampling device and possible dehydration of exhaled particles. This result emphasizes the necessity of exact humidity and temperature control during the sampling of exhaled human breath.

Plate 16 illustrates the sampling arrangement used for experiments of this kind. Cascade impactors inside a heated area are maintained such that there is no humidity change during the passage of exhaled breath through them. Outside the heated area the ambient aerosol impactors may be used without humidity adjustment if the ambient humidity is high; otherwise prehumidification of the incoming airstream is required.

Plate 16 shows the results of the sampling of automotive lead aerosol under conditions of high outdoor humidity (during rain). The lead concentration data, as well as data from a similar chalk dust experiment, can be used to calculate the concentration ratio exhaled/ambient. This ratio is a measure of the fractional deposition on inhalation for each particle size range. Minimum deposition is clearly seen for impactor

Plate 15

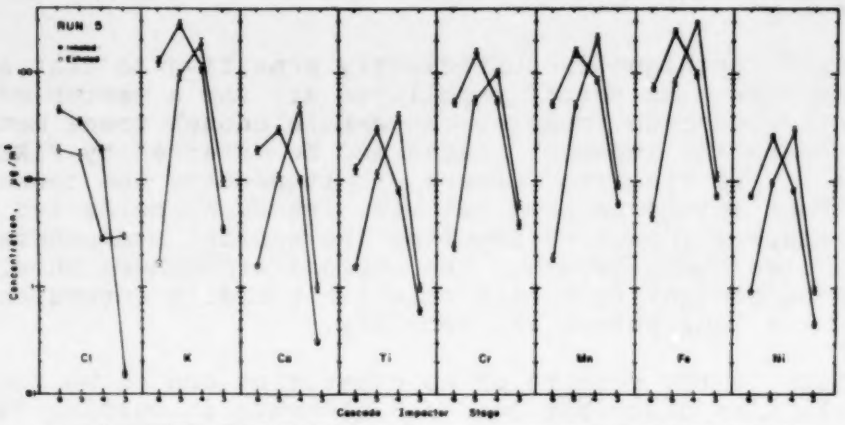



Fig.6(a). Particle size distributions of trace elements in inhaled and exhaled air for Run 5. Metallic elements generally show a shift toward larger particle sizes in exhaled air.

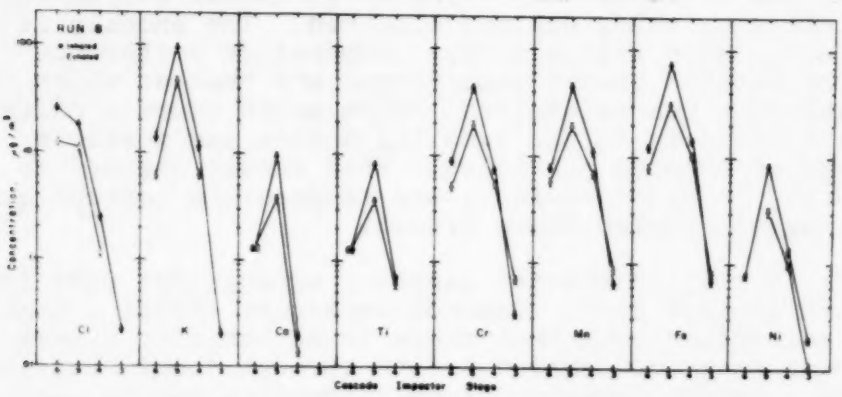



Fig.6(b). Particle size distributions of trace elements in inhaled and exhaled air for Run 8. No systematic shift toward larger sizes is found, and exhaled concentrations are generally lower than inhaled.

Source: A-25.
K. Roland Akselsson, Georges G. Desaedeleer, Thomas B. Johansson, and John W. Winchester, Particle size distribution and human respiratory deposition of trace metals in indoor work environments, Annals of Occupational Hygiene, 19, 225-238, 1976.

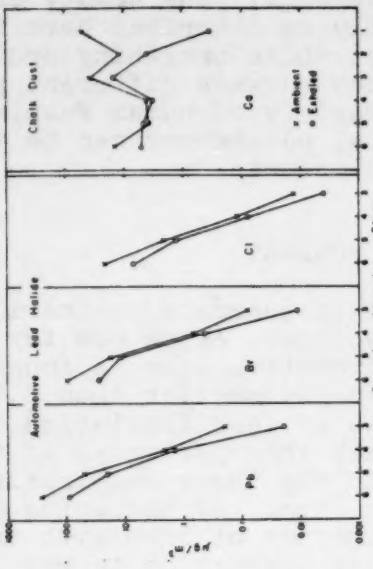



**Figure 2.** Concentrations as a function of particle size for separate automotive exhaust and chalk dust experiments
Small cascade impactors (1 L/min air flow) were used for all data points except for Pb, Br, Cl on stages 4 and 3 where large impactor data (12 L/min air flow) were used. Exhaled air (O) deficit below ambient air (X) represents particle loss during breathing. Analytical errors of relative concentrations are less than the sizes of the plotted points

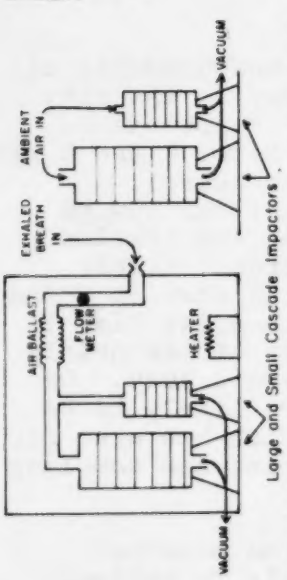



**Figure 1.** Diagram for simultaneous sampling of exhaled and ambient aerosols, showing air ballast arrangement for constant sampling flow rate, temperature regulator for humidity control, and flow meter for breathing rate regulation

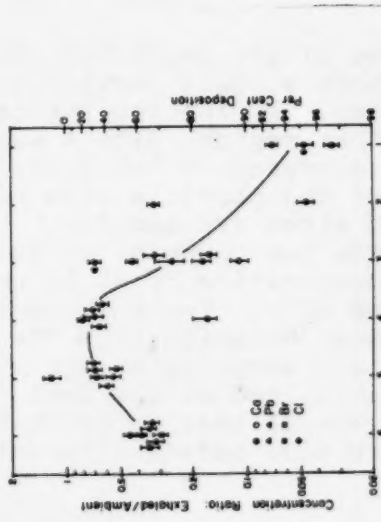



**Figure 3.** Concentration ratios as a function of particle size for simultaneous exhaled and ambient samples
Solid points are for separate automotive exhaust and chalk dust experiments; open points are for a mixed experiment. Pb, Cl, Br data for stages 6 and 5 by small impactor, stages 4 and 3 by large impactor; Ca data by small impactor except where marked by *. Error bars represent absolute standard deviations in the ratios

Source: B-18.
Georges G. Desaedeleer and John W. Winchester, Trace metal analysis of atmospheric aerosol particle size fractions in exhaled human breath, Environ. Sci. Technol., 9, 971-972, 1975.

stages 5 and 4 encompassing the diameter range 0.25-1 μm, a result which is in close agreement with model calculations and experiments with synthetic aerosols. The beauty of being able to measure this curve directly as described here is that it can easily be accomplished while breathing ordinary polluted air. Possible differences between different polluting elements can be examined, and a variety of human respiratory parameters as well as environmental parameters can be tested for actual atmospheric aerosol pollutants.

## THE FATE OF LEAD AEROSOL ALONG A ROADWAY

Along a roadway lead aerosol is generated primarily by automobiles which burn leaded gasoline. As we saw for the city of St. Louis, most of the automotive lead is found in the very smallest particles, typically smaller than 0.25 μm aerodynamic diameter. The studies of lead inhalation described in the previous paragraphs indicate that particles of this size are more likely to be deposited in the lower respiratory tract than particles somewhat larger in size. By comparing measurements of the particle size distribution of lead with those of the efficiency of deposition during inhalation we may estimate, as a function of particle size, the overall deposition of lead which occurs in the atmosphere as it enters the respiratory tract.

In Plate 17 are presented the results of measurements at three locations along a heavily traveled roadway in the city of Los Angeles. During the typical afternoon crosswinds blowing in that region, Site A was upwind and Sites C and D were immediately downwind of the traffic lanes. The overall appearance of the particle size distributions at the upwind and downwind sites are similar. However, close examination shows that the two downwind sites have a measurably higher relative concentration of <0.25 μm diameter lead than is found at the upwind site. For the downwind sites the aging time is shorter between emission from the exhaust pipes of the nearby automobiles and sampling at the sites a few meters away. On the other hand, lead at the upwind site is more likely to be due to the general lead aerosol in the city which has aged for a much longer time between its automotive sources and sampling at the site.

These results may be used together with the measured deposition efficiency curve described previously to estimate an overall lead fraction deposited in the respiratory tract. At downwind sites C and D fifty percent more of the stage 6 (particle size class 6) lead is deposited in thr respiratory tract than for the upwind Site A. Differences also exist for the larger particle size classes. Thus the total concentration of lead in the atmosphere is only approximately indicative of

Plate 17

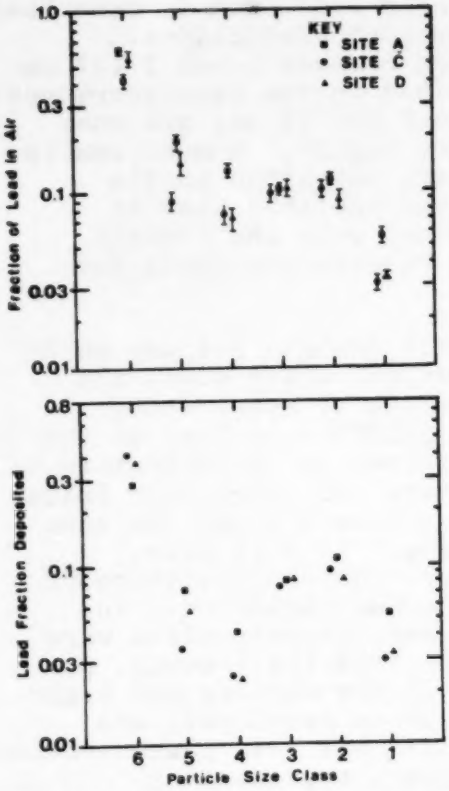



Fig. 2. (a) Particle size distribution of lead aerosol, normalized to 1 $\mu$g Pb $m^{-3}$, at the upwind site (site A) and downwind sites (sites C and D).
(b) Fraction of the atmospheric lead at the upwind and downwind site deposited into the respiratory tract as a function of particle size.

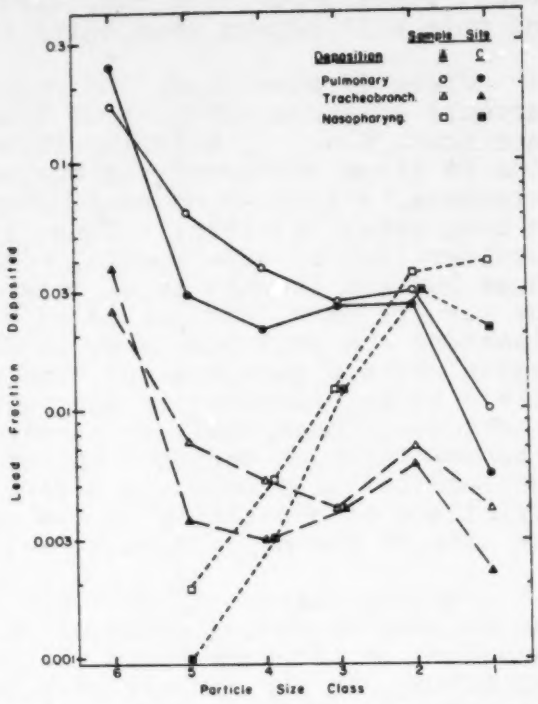



Fig. 3. Predicted deposition efficiencies for lead aerosol at 35 m upwind (A) and 8 m downwind (C) sites along a Los Angeles freeway, using particle size distributions for lead at the two sites measured by PIXE and published deposition curves for three regions of the human respiratory tract.

Source: B-20.
Georges G. Desaedeleer, John W. Winchester, and K. Roland Akselsson, Monitoring aerosol elemental composition in particle size fractions for predicting human respiratory uptake, Nuclear Instruments and Methods, 142, 97-99, 1977.

the amount of deposition one can expect in the respiratory tract, since deposition must also depend upon particle size, and this will depend upon aging time in the atmosphere.

Plate 17 also shows the results of combining the measured particle size distribution of lead at two of the sampling locations, A and C, with the theoretical predictions for deposition in three different regions of the respiratory tract: pulmonary, tracheo-bronchial, and naso-pharyngeal (Task Group on Lung Dynamics, 1966). These theoretical curves have not been verified by experimental methods for lead such as described above but are assumed to be reasonably good predictions. The results show that particles of size classes 1 and 2 (>2 μm diameter) are most likely to be deposited in the naso-pharyngeal region whereas particles of size class 6 (<0.25 μm) are most likely to be deposited in the pulmonary region. A much smaller fraction of these smallest particles are deposited in the tracheo-bronchial region. Therefore the particle size of the lead in the atmosphere determines not only the overall efficiency of deposition in the human respiratory tract but the site of the deposition as well.

Another feature of the lead aerosol along a roadway which can be used as an indicator of lead aerosol aging time, and therefore be of interest in the prediction of respiratory deposition, is the content of bromine relative to lead in the aerosol. Plate 18 shows the time variation in concentration of lead and in the bromine/lead ratio, every two hours from Friday until Monday, September 13-16, 1974, at Site A along the same Los Angeles freeway discussed previously. At this site, which was upwind during afternoon hours, the concentration of lead on a 24-hour basis exhibited a diurnal variation. In the afternoon "upwind" condition the lead concentrations were very low and represented lead, not just from the freeway, but mostly from other parts of the city. In the morning and night times a crosswind in the opposite direction developed, and Site A became "downwind." At these times the lead concentration reached values more than ten times higher, representing primarily relatively young lead aerosol generated along the freeway. The bromine to lead ratio also exhibited a diurnal fluctuation. If bromine and lead were equally stable elemental constituents of the aerosol particles generated by automotive emissions, the ratio should be invariant with time and total lead concentration. However, during the times when lead concentrations were highest, and therefore the lead aerosol aging time was shortest, the bromine content per unit of lead is seen to be highest. At other times, when the lead aerosol had been more aged, the bromine content relative to the lead was much less, suggesting that bromine is released from the aerosol during aging.

Plate 18

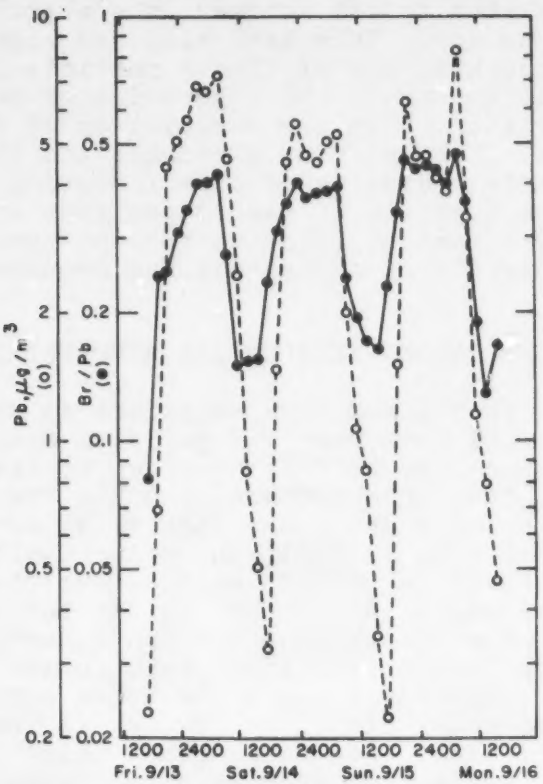



**Fig. 1.** Time-dependent Pb concentration and Br/Pb weight ratio relationships in the Los Angeles aerosol, freeway site A, 1974.

**TABLE I**

**Lead and Bromine Concentrations in Cascade Impactor Particle Size Fractions***

| | Pb, ng/m³ | | | Pb, % mass | | | Br, ng/m³ | | | Br, % mass | | | Br/Pb | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | A | C | D | A | C | D | A | C | D | A | C | D | A | C | D |
| Total | 253 | 2185 | 2207 | | | | 91 | 791 | 707 | | | | | 0.36 | 0.36 |
| Stage 6 | 139 | 1395 | 1243 | 46.2 | 63.9 | 56.3 | 37.8 | 510 | 454 | 41.5 | 64.4 | 64.1 | 0.27 | 0.36 | 0.36 |
| 5 | 41.6 | 157 | 280 | 13.8 | 7.2 | 12.7 | 11.9 | 30.5 | 48.7 | 13.1 | 3.8 | 6.9 | 0.29 | 0.19 | 0.17 |
| 4 | 33.2 | 179 | 177 | 11.0 | 8.2 | 8.0 | <9.2 | 51.9 | 38.3 | <10.1 | 6.6 | 5.4 | <0.28 | 0.29 | 0.23 |
| 3 | 28.9 | 221 | 246 | 9.6 | 10.1 | 11.2 | 8.6 | 92.7 | 77.1 | 9.5 | 11.7 | 10.9 | 0.30 | 0.42 | 0.31 |
| 2 | <28 | 199 | 199 | <9.5 | 9.1 | 9.0 | 10.5 | 82.1 | 64.3 | 11.5 | 10.4 | 9.1 | >0.37 | 0.41 | 0.32 |
| 1 | <28 | <34.5 | 61.6 | <9.5 | <1.6 | 2.8 | 7.4 | 23.9 | 25.3 | 8.1 | 3.0 | 3.6 | >0.26 | >0.69 | 0.41 |

*Aerodynamic diameters, μm, for stages: >4(1), 4-2(2), 2-1(3), 1-0.5(4), 0.5-0.25(5), <0.25(6, filter). % mass for each stage relative to sum of stages. Samples collected at Los Angeles freeway sites A (upwind); C, D (downwind), 1530-1730 Thursday, 12 September 1974.

Source: A-17.
G.G. Desaedeleer, J.W. Winchester, R. Akselsson, and K.A. Hardy, Bromine and lead relationships with particle size and time along an urban freeway, Trans. Am. Nucl. Soc., 21, Suppl.3, 36-37,1975.

These results are consistent with the suggestion already made that, during times when Site A was upwind with air flow from the sampling site to the roadway, the measured lead was of significantly older age. This lead also had significantly lower relative concentration of finest particle lead. The aging process then results both in the liberation of bromine to the atmosphere as a gas and also the coagulation of finest particles into larger sizes. The aging of particles and the increasing of their average particle size is of direct bearing on estimating the efficiency and location of lead deposition in the respiratory tract. The bromine content relative to lead provides a useful indicator of the extent of aging that has occurred.

## LEAD AEROSOL IN THE INDOOR RESIDENTIAL ATMOSPHERE

Lead aerosol from automotive emissions is seemingly ubiquitous and occurs both near and far from automobile traffic lanes. Whereas there may be other sources of lead in an urban atmosphere, automotive lead aerosol, even in the city of St. Louis where smelting and other industrial activities are carried out intensively, is still the major constituent of lead. It is of some interest to know to what extent the lead aerosol in the indoor residential atmosphere is automotively derived and how rapidly the air exchanges between indoors and outdoors to bring lead from the outdoor atmosphere to the indoor environment. In other words, does the house act as a barrier and cleanse the incoming air of lead? Or, is there an indoor source of lead, distinct from automotive, which should be taken into account when estimating average human exposures over a normal day of human activity?

Plate 19 summarizes the results of measurements by streaker samplers made simultaneously indoors and outdoors in a residential neighborhood in Denver, Colorado. During the one week of sampling that was carried out a meteorological change by chance occurred outdoors which provides us with the opportunity of estimating whether indoor sources of lead may exist. On the left hand side of Plate 19 the outdoor concentrations of lead, bromine, and the bromine/lead ratio are presented. During the first and last days of the week, lead concentrations outdoors were at values probably typical for the city. The same was also true for bromine and the bromine/lead ratio. During the middle of the week, however, a several day period was encountered when lead levels at this particular sampling site dropped to very low values. The same was true for bromine, but, owing to the inability to detect bromine much of the time, the bromine/lead ratio was usually indeterminant.

At an indoor location the lead concentrations during the initial and final periods of the week were similar to those

Plate 19

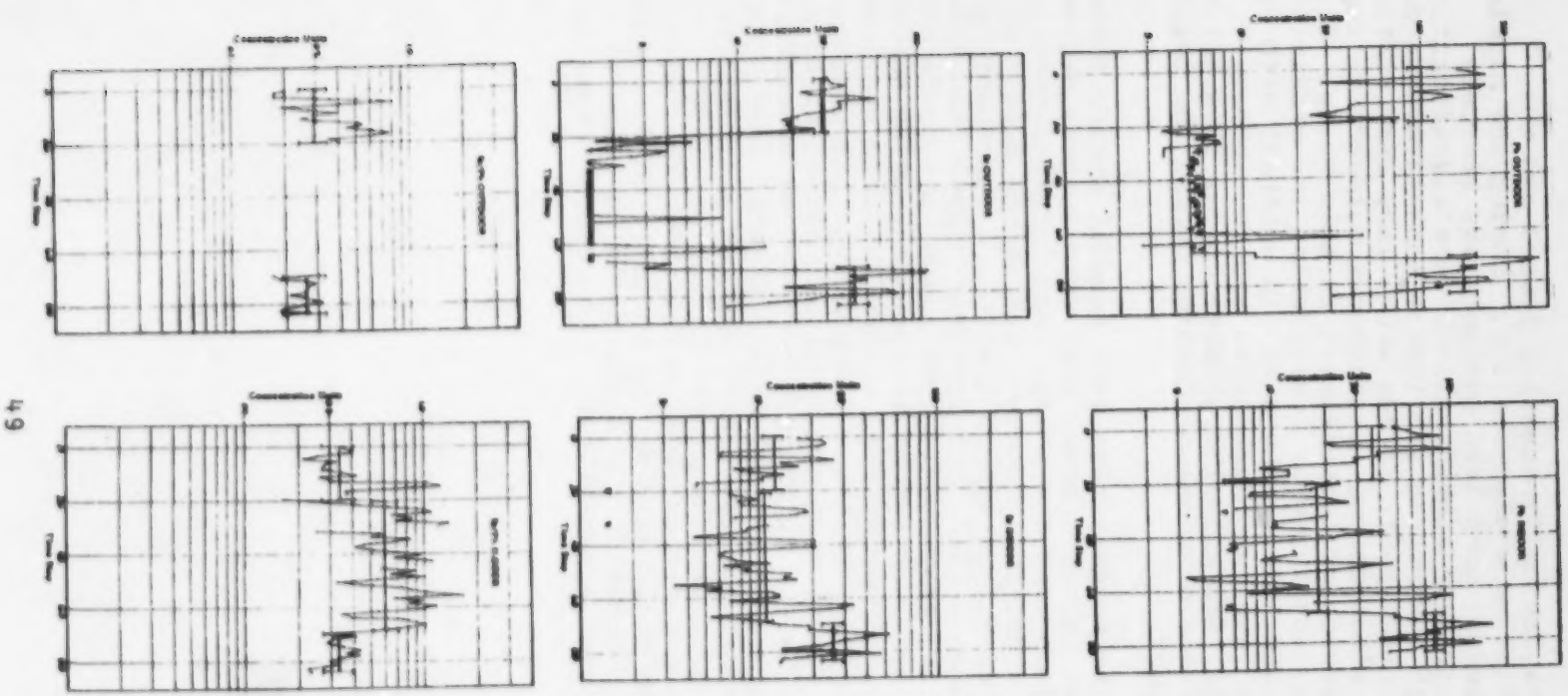


Figure 1. Time variation of Pb and Br concentrations (in relative units) and Br/Pb ratio in Denver single-family dwelling. Time steps represent 2-hour sampling intervals, starting and ending at 1600 hours October 5-12, 1976. Mean values Pb, Br, and Br/Pb for each of three time periods are indicated by horizontal bars, with their standard deviations as vertical bars.

Source: A-23.
D.J. Moschandreas, W. J. Courtney, J.O. Pilotte, J.W. Winchester, H.C. Kaufmann, J.W. Nelson, and R.M. Burton, Indoor and outdoor sources of particulate air pollution in a residential environment, in proceeding, Fourth Joint Conference on Sensing of Environmental Pollutants, 1977.

measured outdoors (actually somewhat lower) and the bromine/lead ratios were also similar. During the middle part of the week, however, when lead outdoors was scarcely detectable, indoor lead concentrations were significantly higher. Although lower than the indoor concentrations during the initial and final parts of the week, they were sufficiently higher than the simultaneous measurements outdoors to suggest that an indoor source of lead existed in this house. The bromine also was only somewhat lower during the middle of the week than early and late in the week, in contrast with outdoors when the bromine level was much less, and the indoor bromine/lead ratio was actually greater during this period than that measured either outdoors or indoors during the beginning and end of the week.

These results suggest that lead aerosol during normal times infiltrates into the house with only a small degree of particle removal so that the indoor lead concentration is similar to that outdoors. However, during the middle of the week the outdoor lead was so low that a secondary indoor lead source, characterized by a somewhat higher than average bromine/lead ratio, prevailed. This source may be secondary entrained dust from furnishings in the house which had become inoculated with, one may assume, automotive lead over many years of occupancy of the house. Normally, this component of lead is a small fraction of the total concentration of lead in the indoor atmosphere. By chance, however, we encountered a time when, because of special meteorological circumstances, the secondary indoor source became dominant and could be discerned. Consequently the indoor living environment can not be assumed to have a simple relationship with the outdoor atmosphere. Some pollutants may be infiltrated from outdoors and some may be generated from within. In the case of lead in the Denver house, apparently both source processes are operative.

## SECTION 7

## AEROSOL TRANSPORT OUT OF THE URBAN SOURCE REGION

In studies of trace metals in the urban atmosphere it is of considerable importance to have a general understanding of the composition of cleaner air. A study of clean air serves both to provide a baseline or reference for comparison of the urban atmosphere, in order to determine to what degree the urban atmmosphere has been polluted beyond natural levels, and also to facilitate the detection of pollutants transported outward from the urban region into cleaner areas. Two case studies are of a special interest in the investigation of urban trace metals in North American cities.

### THE NORTH FLORIDA COASTAL ZONE

North Florida is a region containing small cities and towns and large areas of forested land. Heavy industry is virtually absent, and the quality of air is considered good. Within the eastern United States, north Florida may have an atmospheric composition closer to natural than any other area. Furthermore, the coastal zone is a zone of interaction of maritime and terrestrial influences and provides an opportunity to compare the chemical relationships in these two types of air.

As in the city of St. Louis, we have sought in Florida to determine the relative trace metal composition of the aerosol as a function of particle size. In Plates 20 and 21 trace element concentrations and their ratios, as determined by cascade impactor sampling and PIXE analysis, are presented. These several elements divide naturally into at least three groups: elements associated primarily with soil dust; elements which are anomalously enriched in the atmosphere, including copper and zinc; and the element sulfur, a class by itself, which may be largely due to gas-to-particle conversion into sulfates. The soil dust elements iron, potassium, calcium, titanium, and manganese are very nearly in the ratios in which they occur in natural soils, and all of them occur preferentially on particles greater than 1 μm aerodynamic diameter (impactor stages 3, 2 and 1). This observation is consistent with the dispersion nature of the soil dust source, forming large particles preferentially to smaller

Plate 20

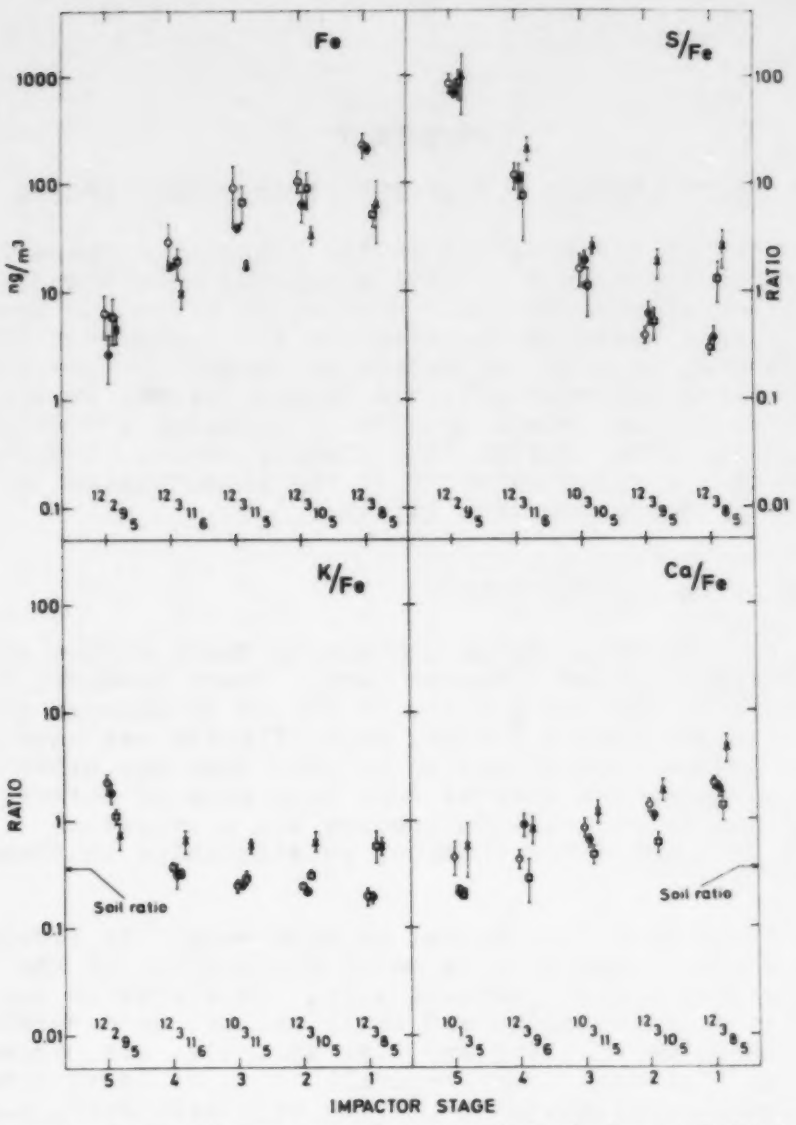



Fig. 3. Arithmetic mean values of Fe concentrations and of weight ratios for other elements to Fe plotted versus impactor stage number, equivalent to a logarithmic scale of aerodynamic particle diameter. The vertical bars represent one standard deviation of the mean of the data set. The numbers at the bottom of each graph show the number of nonzero values included in the averages. Where this number is less than the corresponding number of samples analyzed (Table 1), the element was below detection limit in the remaining analyses. If the element was detected in more than half the number of analyses, a value has been plotted; otherwise, an upper limit value is indicated. Points for city site A are indicated by open circles, for city site B by closed circles, for the forest by open squares, and for the coast by crosses.

Source: B-25.
Thomas B. Johansson, Rene E. Van Grieken, and John W. Winchester, Elemental abundance variation with particle size in north Florida aerosols, J. Geophys. Res., 81, 1039-1046, 1976.

Plate 21

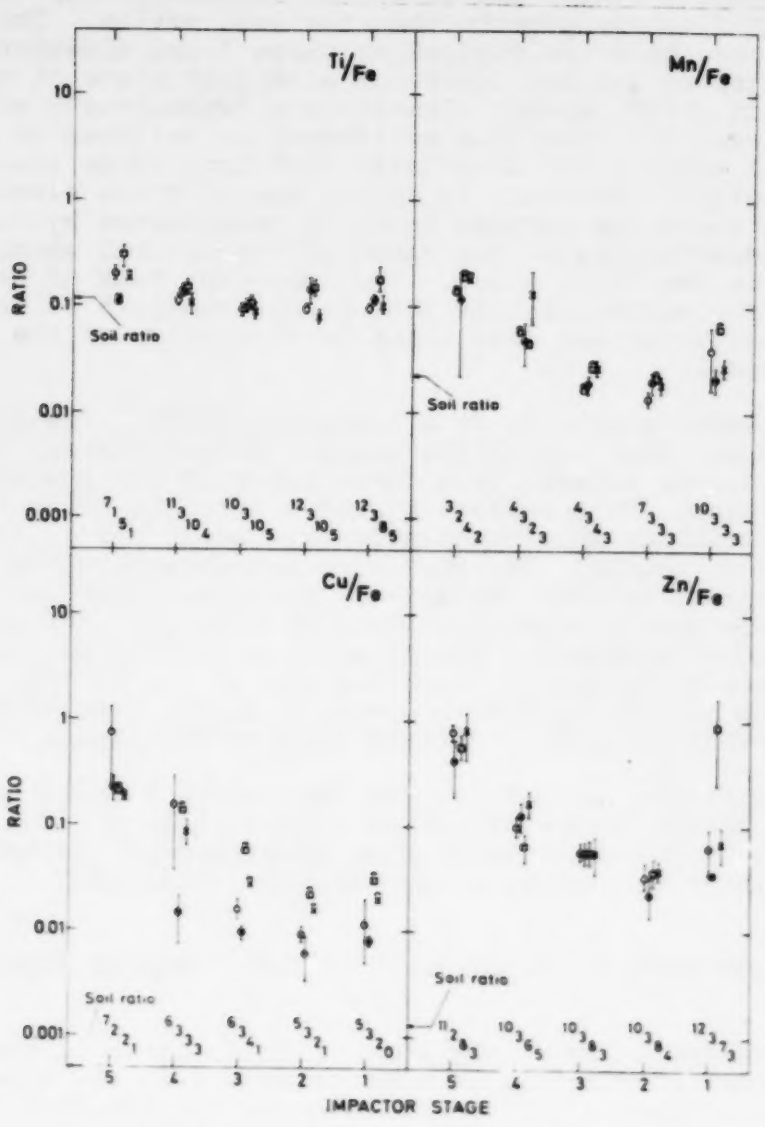



Fig. 3. (continued)

Source: B-25.
Thomas B. Johansson, Rene E. Van Grieken, and John W. Winchester, Elemental abundance variation with particle size in north Florida aerosols, J. Geophys. Res., 81, 1039-1046, 1976.

ones by the mechanical action of wind on rock and soil material.

The elements copper and zinc have concentrations relative to iron significantly greater than the soil ratios. The ratios observed here are typical of those found elsewhere in clean atmospheres and may represent a natural state of the atmosphere in which certain elements are "anomalously enriched." In remote areas the anomalous enrichment is believed to be due to a natural process not associated with long range transport of air pollution. However, to detect one of these elements as a pollutant above the natural level is complicated by our lack of clear understanding of the cause of the natural anomalous enrichment in the first place. The important task of developing techniques for monitoring the long range transport of heavy metal air pollution has been begun by this study of the North Florida aerosol.

The element sulfur is in a class by itself. Present indications are that all of the eastern United States, including north Florida, is covered by a large cloud of air pollution derived sulfate. This sulfate migrates into the north Florida area and diminishes in concentration gradually during transport over longer distances. The particles are in general of very fine size resulting from the gas-to-particle conversion nature of the source process. Thus, as observed, the ratio of sulfur to iron increases strongly with decreasing particle size. Little evidence for local sources of sulfur are observed in the north Florida area when compared to the overwhelming amount of sulfate aerosol transported into the region.

In conclusion, we may say that the north Florida aerosol provides a useful reference of relatively clean air for comparison with more polluted urban atmospheres. However, at least sulfur is already a significant contaminant.

## AIR POLLUTION PRESENT IN THE NORTH ATLANTIC MARINE ATMOSPHERE AT BERMUDA

As with the study of the north Florida aerosol, the particle size distribution of trace elements in the atmosphere of Bermuda provides a useful indicator of the presence of long range transport of air pollution. Bermuda lies some 1500 kilometers southeast of New York and its atmosphere is representative of much of that over the North Atlantic ocean far from the North American continent. Air pollution is not visibly present.

If the aerosol particles are carefully sampled as a function of particle size under a wide variety of wind directions and weather conditions varying from stormy to calm, it

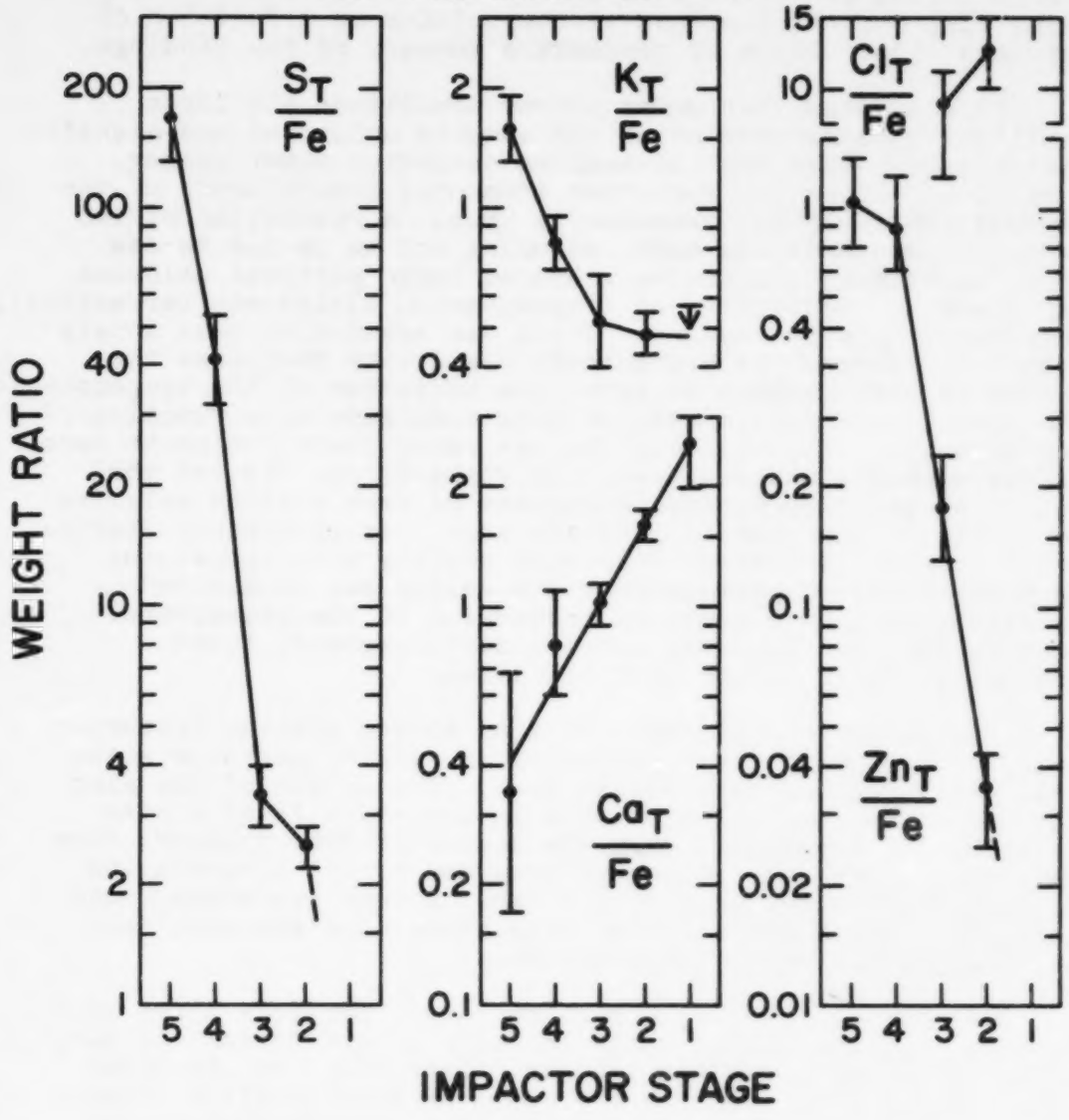
is possible by a regression procedure to resolve the ever-present sea spray component of the aerosol from that of aerosol particles of other sources. In an investigation of this possibility a series of ten cascade impactor samples collected over a period of three weeks in the fall of 1973 were analyzed using PIXE for their elemental composition as a function of particle size. Plate 22 presents a summary of the findings.

It was noted that under stormy conditions the large particle chlorine content of the samples collected was significantly higher than that of samples collected under calmer conditions. However, for other elemental constituents of the aerosol, that was not necessarily true. A resolution of two aerosol components was made, assuming one to be due to sea spray containing all of the measured large particle chlorine and the other consisting of tropospheric, ultimately terrestrial, components typified by iron, which was assumed to come solely from this source. By a graphical regression technique the ratios of each element to iron, the indicator of the tropospheric component, were determined for this component as a function of particle size. In this way the sea spray contribution to each of the elements was resolved. In Plate 22 are plotted the ratios of the tropospheric component of each element relative to iron as a function of particle size. As with north Florida, the sulfur to iron ratio decreased sharply with increasing particle size, suggesting that the sulfur may be derived primarily by gas-to-particle conversion in the atmosphere whereas the iron is a terrestrial dust component found predominantly in larger particle sizes.

The particle size trend of zinc showed similar features, owing to its being found primarily in smaller particle sizes than is typical of terrestrial dust. The origin of the zinc may be natural or pollution, but in any event is of a size distribution suggesting that its source process produces fine particles. One such source process may be the condensation of high temperature vapors, but other source processes could include biogenic evolution of zinc containing aerosol, such as from organic vapor condensation.

Calcium is found as a rule on larger particle sizes than is iron, and the Bermuda data in Plate 22 are typical of many areas including north Florida (cf. Plate 20). On the other hand potassium is found as a rule on smaller particle sizes than is iron (cf. Plate 20). Since the contribution of sea spray related aerosol production has been removed, we examine in Plate 22 only the net tropospheric or terrestrial component of these elements. The large particle size preference for calcium over iron may be due to the nature of the dispersion mechanism which generates calcium-bearing aerosol, such as the dispersion of calcite, from that of iron which may be derived from different clay mineralic constituents of soil. In the

Plate 22




Source: B-28.
Dennis L. Meinert and John W. Winchester, Chemical relationships in the North Atlantic marine aerosol, J. Geophys. Res., 82, 1778-1782, 1977.

case of potassium, the significant enrichment over iron in the smallest particle sizes is as yet an unexplained observation. A biogenic source of fine potassium containing aerosol is suggested.

Studies elsewhere in the world indicate that the sulfur content observed in fine particles in Bermuda is by no means typical of the marine atmosphere. Sulfur in the aerosol sampled at Bermuda is predominantly in the sub-micron particle sizes, not the coarse particles greater than 1 μm and typical of sea spray, and it now appears that the fine particle sulfur is mainly due to long range transport of air pollution from the continental areas 1000 km or more distant. The comparative study of urban with the maritime atmosphere suggests that particulate materials may be transported over considerable distances and contaminate atmospheres far from their sources. In the case of sulfur the strength of pollution sources is sufficiently great so that the pollution effect can be seen as far from the North American continent as Bermuda. Whether this is also true for trace metals has not yet been determined. However, by extending investigations of this kind we may gain a sharper understanding of the potential for the remote atmosphere to be contaminated with any air pollutant. Studies of apparently clean air serve as an important complement to studies of the urban atmosphere in understanding the impact of man's activities on the atmospheric environment as a whole.

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